

Chemistry with a super-twist: A molecular trefoil knot, part 1.

Henry Rzepa 

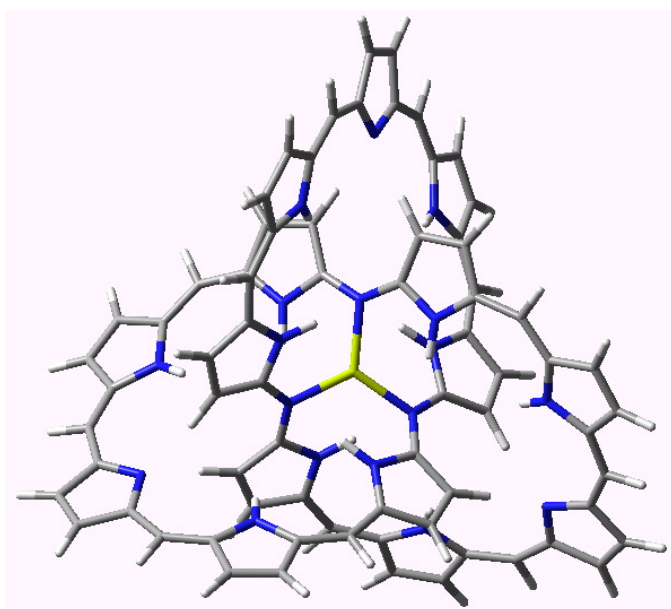
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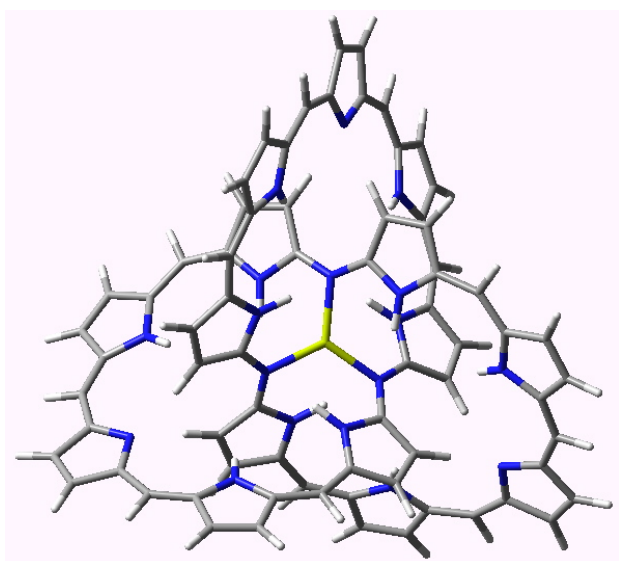


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Something important happened in chemistry for the first time about 100 years ago. A molecule was built (nowadays we would say synthesized) specifically for the purpose of investigating a theory. It was cyclo-octatetraene or $(CH)_8$, and it was made by Willstätter and Waser[cite]10.1002/cber.191104403216[/cite] to try to find out if benzene, $(CH)_6$, was an **aromatic** one-off or whether it might be a member of a series, envisaged as $(CH)_n$. Of course, a hell of a surprise was in store for Willstätter and Waser[cite]10.1002/cber.191104403216[/cite]! Prior to this synthesis, $(CH)_8$ had never existed; nature had not gotten there first. In that sense, chemistry became much like mathematics had before it; it was OK to make molecules because they *might be interesting*, and for the purpose of investigating possible patterns in nature. So it is in this spirit that I suggest an interesting molecule here. It is a molecular trefoil, constructed by joining 15 pyrrole units together into a ring with appropriate linkers and in effect tying a knot in that ring. A trefoil knot to be specific.



A molecular trefoil knot, shown with a Mg at the centre. Click to view in 3D

Why might such a molecule be interesting? These are **ten reasons**:

1. It would make an interesting ligand for a metal
2. It has lots of interesting groves and dimples for transition states to nest in
3. It would be an extended porphyrin (a pentadecaphyrin to be precise). Nature likes to make molecules out of tetraphyrins (chlorophyll, haemoglobin, etc), and so we are pushing beyond nature's own boundaries. Both a penta and a hexadecaphyrin have already been made[cite]10.1002/chem.200701909[/cite],[cite]10.1002/chem.200701909[/cite],[cite]10.1021/ja005588o[/cite]
4. The trefoil knot is a most interesting object in a branch of mathematics called **knot theory**, and it is also related to another fascinating object, the **Möbius band**.
5. The pyrrole units in such a molecule are *conjugated* via the π -system, and the molecule above is potentially fully conjugated across its entire length. This could make it aromatic,

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and hence it is interesting for the same reason that Willstätter[cite]10.1002/cber.191104403216[/cite] found cyclo-octatetraene so.

6. The system above, if carefully counted, would have 74 π -electrons in cyclic conjugation. This would make it a $4n+2$ aromatic ($n=18$), just like benzene, but not at all like $(\text{CH})_8$ (which as Willstätter and Wases[cite]10.1002/cber.191104403216[/cite] found, is not aromatic).
7. It seems highly twisted. Indeed the title of this post is super-twisted. But is it really? We learn from topology that twist is not the only property that cyclic bands or strips can have. They can also exhibit **writhe**. So is it writhed as well as twisted?
8. Aromatic molecules have one rather mysterious behaviour. The ring bonds in in such systems resemble neither double nor single bonds, but aromatic bonds, and in this they have a length intermediate between the single and the double, and this applies to all of the bonds. The origins of this *delocalization* continue to provoke controversy (see [this post](#)). Thus it is thought that only (planar) carbon rings with around 26 or less π -electrons can exhibit such equal lengths (boron rings can apparently go much further. [cite]10.1039/B911817A[/cite]). More than that, and distortion sets in which makes the lengths alternate. The molecule above has 74 π -electrons. What will its bonds do, and is what they do related to the twist (or the writhe) of the system?
9. The trefoil is **chiral**. It cannot be superimposed upon its mirror image. But how chiral (whatever that means)?
10. The system has many design handles, including the number of pyrrole (or thiophene) units, the number of N-H vs =N motifs, and the scope for templating using a metal cation (Mg in the example above).

So what might be the properties of our trefoil knot? I am going to list only two here.

1. A theorem emerged from mathematics in the 1970s known as the White, Călugăreanu, Fuller Theorem. It defines the topological properties of bands in terms of a quantity known as the linking number (Lk). The theorem states that: **Lk = Tw + Wr**, where Lk is an integer, being the sum of two properties **Tw** (the total twist of the band) and **Wr** (the total writhe of the band). This theory was recently extended to the analysis of twisted conjugated molecular rings[cite]10.1021/ja710438j[/cite], for which Lk adopts integer values (in units of π). Thus a conjugated Möbius π -cycle has a value $Lk = 1\pi$ (specifically when describing the band formed by the π -electrons). Most of this value is composed of twist rather than writhe. What of our molecule? Well, it has $Lk = 6\pi$, and this comprises $Tw = -0.8\pi$ and $Wr = +6.8\pi$ (yes the two can be either positive or negative, and do not have to be the same sign). The surprise is that it is (overall) hardly twisted! The knot is composed almost entirely of writhe. So much for the title of this post!
2. What about the bond lengths? The best way of analyzing these[cite]10.1021/ol703129z[/cite] is to compare pairs of so-called *meso*-bonds, being the coupler unit connecting any two pyrrole rings. Around the cycle, all the C-C meso-pairs are $\sim 1.4\text{\AA}$ and the C-N pairs are both $\sim 1.34\text{\AA}$. That characteristic of benzene, in having all its (C-C) bonds equal, seems true here as well (at least at the B3LYP/6-311G(d,p) level, see e.g. [10042/to-2109](#)). There are reasons for thinking that in fact the B3LYP method does predict this behaviour more or

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less realistically). By the way, a molecule with a π -linking number of six is indeed classified by the same selection rule as benzene, ie $4n+2$ (odd numbers of Lk are governed by a $4n$ rule instead).[cite]10.1016/j.comptc.2014.09.028[/cite]

It is tempting to conclude that perhaps the extended conjugation of this molecule (shown by the bond length equality) is somehow connected to the dominance of writhe over twist in this trefoil.

I will follow this post up with another relating to the predicted chiro-optical properties. For now, I leave its synthesis to be contemplated by a present day Willstätter or Waser.

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