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Abstract:
Molecules with a π-system that can be mapped onto a Möbius band may display Möbius aromaticity. Such molecules are difficult to synthesize because they have a twisted structure. Recently, we combined chiral [6]helicene and fluorescent [7] cycloparaphenylene and synthesized the first helicene para-phenylene ([6,7]HPP) carbon nanohoop. We have demonstrated that this design strategy ultimately provides Möbius topology of the molecular π-electron system and, therefore, offers the potential to study Möbius aromaticity experimentally. In addition, the synthesized nanohoop exists as a mixture of conformers in a solution. Some of the conformers possess a different orientability of their π-systems, i.e., they differ in their topology. As a result, the recorded circularly polarized luminescence of isolated enantiomers displays both the left and right handedness of the emitted light, each emanating from a conformer with different π-system topology. Therefore, [6,7]HPP provided the first experimental evidence of such topological bistability in carbon nanohoops.

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Topological Bistability of the $\pi$-System in Helicene Carbon Nanohoop

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Abstract Molecules with a $\pi$-system that can be mapped onto a Möbius strip may display Möbius aromaticity. Such molecules are difficult to synthesize because they have a twisted structure. Recently, we combined chiral [6]helicene and fluorescent [7]cyclopentaphene and synthesized the first helicene para-phenylene ([6,7]HPP) carbon nanohoop. We have demonstrated that this design strategy ultimately provides Möbius topology of the molecular $\pi$-electron system and, therefore, offers the potential to study Möbius aromaticity experimentally. In addition, the synthesized nanohoop exists as a mixture of conformers in a solution. Some of the conformers possess a different orientability of their $\pi$-systems, i.e., they differ in their topology. As a result, the recorded circularly polarized luminescence of isolated enantiomers displays both the left and right handedness of the emitted light, each emanating from a conformer with different $\pi$-system topology. Therefore, [6,7]HPP provided the first experimental evidence of such topological bistability in carbon nanohoops.

Key words Circularly polarized luminescence; Möbius Aromaticity; Molecular Topology; Carbon nanohoops; Cycloparaphenylene; Helicenes

In 1964, Heilbronner published a seminal paper describing a new type of aromaticity.¹ Using Hückel theory, he predicted that twisting the $\pi$-electron system of [n]annulenes with their 4m $\pi$-electrons into the shape of a Möbius strip should provide a closed-shell system with no loss of resonance energy. Although Heilbronner avoided labelling such a system as aromatic, his prediction clearly suggested its equivalence to the well-established aromatic molecules that follow the Hückel (4m+2) $\pi$-electron rule. This report sparked immense interest in the scientific community and initiated a search for molecules to put the hypothesis to an experimental test.

However, synthesizing a molecule with such an unusual feature of its $\pi$-system is no easy task! Therefore, such molecules were first investigated in silico. For instance, Möbius isomers of coronene,² [n]kekulenes,³ allenes,⁴ cyclacenenes,⁵–⁷ and others⁸ were found as minima on their respective potential energy surfaces but none of these molecules was experimentally observed to this date. Cyclononatetraenyl cation was the first species that showed experimental evidence of Möbius aromaticity,¹⁰¹¹ but this finding escaped the attention of the authors at the time due to its reactive nature. The Möbius aromaticity of this carbenium ion was confirmed only later in a computational study.¹² Other Möbius [n]annulenes were investigated only computationally.¹³–¹⁷

It took almost 20 years until Walba synthesized the very first molecular Möbius strip.¹⁸ Although it represented a major step forward, this molecule possessed no $\pi$-system and, therefore, could not demonstrate Möbius aromaticity. Constructing a conjugated molecule into a twisted macrocycle introduces a considerable strain into the structure and diminishes the overlap...

Figure 1 (a) Design concept to realize a Möbius aromatic system implemented in the synthesis of (b) the extended annulene 1, which exists as several (c) Möbius (left) and Möbius (right) diastereomers. Two enantiomers of one of the Möbius 1 diastereomers are displayed.
of the $p_z$ orbitals at the same time.$^9$ The latter is a requirement for electron delocalization to achieve aromatic stabilization. Therefore, small $n$-annulenes$^{13,15}$ are predicted as non-aromatic. Synthesis of larger macrocycles alleviates such issues. However, larger $n$-annulenes are flexible and less-strained isomers with Hückel topology typically dominate in the mixture.$^{19}$

Nevertheless in 2003, Herges and coworkers developed a synthetic strategy that allowed for the synthesis of the first stable Möbius π-extended [16]annulene derivative 1 (Figure 1).$^{20}$ The synthetic strategy relies on combining moieties that display different types of π-electron conjugation: (i) A planar/“normal” as seen in benzene, and (ii) a radial/in-plane as in carbon nanotubes.$^{8}$ It is the latter that leads to twisting the π-system and localizing most of the strain (Figure 1a).$^{21}$ Theoretical prediction suggested that bianthraquinodimethane embedded in an oligoene system with (F)- or (Z)-double bonds provides several Möbius isomers lower in energy than the Hückel isomers (Figure 1b). The synthesis yielded five isomers of 1, three of which could be characterized by single crystal X-ray diffraction (SC-XRD, Figure 1c) analysis.$^{22}$ Both types of isomers of 1, i.e., with the twisted (Möbius) and the non-twisted (Hückel) “topologies”, were isolated and allowed for a direct comparison of the two. The molecular properties that emerge from the aromaticity in Möbius 1 could be observed supporting the prediction of Helfricher although the aromatic stabilization in 1 is rather weak.$^{23}$

A closer look at the two isomers of 1,$^{20}$ however, reveals the rather unfortunate use of the term Möbius/Hückel topology to describe the structure of this and other analogous molecules in the literature. Topology was translated to chemistry by Frisch and Wasserman,$^{24}$ who also introduced terms topological isomerism and topological chirality. As an example, a catenane and a pair of rings (Figure 2a) have different topologies because no geometrical deformation can interconvert them. Instead, breaking and reforming a bond is necessary to accomplish such transformation.$^{25}$ Similarly, a topologically chiral molecule has no topologically allowed transformations between its enantiomers. For example, the mirror images of a trefoil knot are topological enantiomers because no deformation can interconvert them (Figure 2a).$^{26}$ Therefore, the Möbius and Hückel isomers of 1 are homeomorphic, i.e., topologically equivalent, because both can be interconverted via structural deformations.$^{27}$ Moreover, the separated enantiomers of a chiral Möbius isomer of 1 could racemize$^{22,28}$ without the need to break any bonds. Such structures thus display the topology of a circle and can be labelled as topologically trivial.$^{29}$ In fact, it is the odd number of phase inversions in the π-electron system that defines a potentially Möbius aromatic molecule, a feature that can be achieved without mapping it onto a Möbius strip.$^{30}$ The examples of the in-plane Möbius aromatic cyclopropane$^{30}$ or Möbius antiaromatic [6]helicene radical anion$^{29}$ demonstrate the point (Figure 2b).

It is, however, conceptually useful to think about polyaromatic hydrocarbons (PAHs) in terms of the orientability of their π-electron system. Orientability is a topological property of surfaces, and the π-electron system of benzene, for instance, can be considered as an orientable 2D surface. A Möbius strip possesses a non-orientable surface, which is now relatively straightforward to translate into the required shape for a curved PAH that can be synthesized and studied. Accordingly, we recently reported the first helicene para-phenylene (HPP) 2 (Figure 3).$^{31}$ Formation of 2 can be formally envisaged as an insertion of a [6]helicene into a [7]cycloparaphenylene. For this reason, we label 2 as [6,7]HPP. The [6]helicene possesses the planar type of π-electron conjugation, while the [7]cycloparaphenylene the radial type. Each of these non-planar moieties helps to distribute the ring strain in the molecule more evenly and allows for a relatively high-yielding synthesis from common building blocks. A computational analysis of the molecular structure of 2 prior to its synthesis suggested that the lowest-energy conformer had a non-orientable π-electron cloud, i.e., it could be mapped onto a singly-twisted Möbius strip (Figure 3a). The presence of the C-C single bond in 2, however, allows for a relatively rapid rotation of the phenylene adjacent to the [6]helicene converting the Möbius conformer into a Hückel conformer ($\Delta G \approx 5$ kcal mol$^{-1}$, DFT, Figure 3b). The latter has an orientable π-electron cloud. This rotation represents a topologically-allowed deformation and categorizes 2 as a topologically trivial object.$^{29}$ Nevertheless, the π-electron systems that are mapped onto the two conformers of 2 differ in their orientability, i.e., they are topologically different. Note that we explicitly distinguish here the topologies of the conformers (3D objects) and those of their π-electron systems (2D surfaces).

To clarify the use of topology for curved PAHs further, we adopt the terms single-stranded and double-stranded Möbius (ssM and dsM, respectively; Figure 2c) molecules coined in a recent review by Guo and Stoddart$^{34}$ to distinguish the topologically non-equivalent classes of compounds that can, however, both display a non-orientable surface of π-electrons. Thus, both 1 and 2...
belong among ssM molecules, while Möbius molecular belts\(^\text{34,35}\) are dsM molecules. Clearly, the topological bistability of the \(\pi\)-electron system that changes the number of its phase inversions can only be realized in the ssM, but not in the dsM molecules.

Similarly, 2 is chiral and successfully separated its enantiomers by HPLC and characterized them unequivocally by electronic circular dichroism and circularly polarized luminescence (CPL). HPP 2 is a chiral luminophore with a moderate luminescence dissymmetry factor of 2.2\(\times10^{-3}\). The measured brightness of CPL, \(R_{\text{CPL}}\) = 63, is relatively high compared to other chiral carbon nanohoops\(^\text{36-41}\) and superior to known [6]helicene derivatives.\(^\text{42-44}\) The configurational stability endowed to the enantiomers of 2 by the presence of [6]helicene in the structure did not allow us to experimentally observe a racemization of the enantiopure samples even upon heating. The computational model, however, clearly showed that their interconversion can be achieved by structural deformation similar to the enantiomerization process observed in plain [6]helicene. Again, unlike dsM structures, the ssM molecules are not topologically chiral.

Although the dsM molecules are topologically stable and more complex, the topological bistability of the \(\pi\)-system in the ssM PAHs could allow for a more straightforward exploration of the effect of the \(\pi\)-system topology on the molecular properties and dynamics. For example, two distinct experimental outcomes could, in principle, be achieved within the same compound upon a change of conformation. This has already been observed by \(^1\)H NMR spectroscopy in porphyrinoids\(^\text{45-47}\) but not yet in PAHs.

The crystal structure of 2 confirms that its \(\pi\)-system is non-orientable and the molecule thus adopts the shape of a Möbius strip (Figure 3a). Can 2, however, transform the orientability of its \(\pi\)-system by assuming a Hückel conformation in solution?

We recorded a series of \(^1\)H NMR spectra as a function of temperature and observed that the individual phenylenes in 2 can rotate on the NMR timescale. The temperature required to reach coalescence for different phenylenes was in good agreement with the distribution of the strain in 2. It is more localized in the more quinoidal phenylenes distant from the helicene, and these also displayed higher barriers of rotation. The experimental free energy for the phenylenes adjacent to the helicene matched our DFT calculations (~8 kcal mol\(^{-1}\)) very well. In order for these phenylenes to turn by 180°, they must first reach the Hückel conformation (Figure 3b). Because of the energy difference, the population of the Hückel conformer is too low to be directly observed in the \(^1\)H NMR spectrum. Nevertheless, we gathered the first evidence that the two topologies of the \(\pi\)-system lead to unprecedented CPL.

A close inspection of the CPL spectra of the individual enantiomers of 2 reveals a relatively minor band at the blue side of the spectrum (Figure 4). This minor band displays the opposite sign of the luminescence dissymmetry factor \(g_{\text{ssM}}\) than the major emission band, i.e., the opposite handedness of the emitted light. We optimized the two lowest-energy excited states of Möbius 2 to determine the sign of the \(g_{\text{ssM}}\) but the sign was the same in both. Therefore, the blue-shifted signal does not originate from a higher excited state of Möbius 2. However, optimization of Hückel 2 in the excited state provided a potential energy minimum, from which the luminescence displays the opposite sign for \(g_{\text{Hückel}}\) and the correct energy shift observed in the emission. Note that the short excited-state lifetime does not allow for rotation of phenylenes in the excited state and the steady-state CPL spectrum thus reflects the ground-state distribution of the conformers in the sample. Considering the computed energy difference between Möbius and Hückel 2, the predicted oscillator strengths of the individual transitions, and assuming the same luminescence quantum yields of the two conformers, the expected ratio of the two bands corresponds reasonably to the integrated spectral intensities in the CPL spectra.

[6,7]HPP thus represents the first example of a PAH where such experimental evidence of the topological bistability of the \(\pi\)-electron system has been collected. Yet, additional model compounds to construct structure-property relationships strengthening the argument are necessary. Possibly, such compounds might allow for developing a strategy to control the handedness of CPL. Switching of the handedness of the CPL using external stimuli in polymers\(^\text{46,49}\) supramolecular assemblies\(^\text{50-56}\) and liquid crystals\(^\text{57}\) was reported. However, such switching by a conformational change in a small organic luminophore has not been accomplished yet. If an external stimulus could switch between different topologies, one might create a brand-new type of molecular optical switches. So far, we can control only the ratio of the two conformers by temperature, while a good molecular
switch for any practical application in optoelectronic devices should be ideally switchable by a quantitative redox process or a photon absorption at room temperature.

HPP 2 was also investigated by others theoretically for two-photon absorption properties.58,59 There is a few analogs ssM PAHs in the literature.32-34 However, the effect of the π-system topology on molecular properties, such as (hyper)polarizability, was studied only computationally in these compounds. For example, Liu and Lu investigated different conformations of phenanthroline carbon nanohoops (Figure 2C, left) with different number of p-phenylenes and found only a minor effect of the topology on the computed properties.64

The aromaticity in the ssM carbon nanohoops has also been studied only computationally. Generally, the weak π-electron conjugation in the neutral nanohoops hampers any measurable effect of (anti)aromaticity. Indeed, [n]cylopophenylenes ([n]CPPs) themselves require 2-electron oxidation to strengthen the π-electron conjugation such that an induced diatomic ring current in [n]CPPs shifts the H1 resonances of the phenylene protons significantly.65,66 In the case of 2, the conjugation pathway across its macrocyclic structure possesses an odd number of carbon atoms, i.e., odd number of π-electrons. As a result, 2 is unable to display Möbius (anti)aromaticity even upon 2-electron oxidation as we confirmed by DFT calculations.31

In summary, we hope that we succeeded in using this perspective as a platform to clarify the somewhat conflicting language that we found to segue from the topic of aromaticity to molecular nanotopology. The terms used relatively loosely in the former due to historic reasons are regarded with rigour in the latter and can sometimes lead to confusion. We used the first helicene carbon nanohoop [6,7]HPP synthesized recently by us to demonstrate this point, and to highlight the effect of the orientability of the π-electron system in this single-stranded Möbius polyaromatic hydrocarbon on its properties. We demonstrated that the trivial topology of [6,7]HPP allows for the topological bistability of the π-electron system via a simple conformational change. In [6,7]HPP, this leads to change of the sign of the luminescence dissymmetry factor, i.e., the sense of rotation of circularly polarized light, a feature not yet observed in the family of related carbon nanohoops. Unfortunately, the use of [6]helicene to endow the enantiomers of [6,7]HPP with configurational stability prevents this compound to display a global (anti)aromaticity, even when oxidized. The reason is the conjugation path in [6]helicene that spans an odd number of carbon atoms. Therefore, we proposed to use [5]helicene that offers conjugation paths with an even number of carbon atoms and synthesize members of [5,n]HPP family. These molecules could allow for (i) exploring the effect of the nanohoop size on the topological bistability and the ensuing chiroptical properties, and (ii) testing the concept of aromaticity at the same time. To our satisfaction, the synthesis of the first two representatives of the [5,n]HPP family, namely, [5,6]HPP and [5,7]HPP, have already been successfully accomplished in our laboratory.

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Conflict of Interest
The authors declare no conflict of interest.

References


(19) There are 2250 conceivable cis/trans isomers of [16]annulene and that the most stable Möbius one is number 137 in the list of the most stable isomers.


(27) Heilbrunner cleverly avoids the use of the term topology as the author may have been aware that the connectivity of atoms in [n]annulenes is the same regardless of their molecular shape, but he may have unintentionally planted the seed of confusion as he used the term “topological equivalent” when illustrating the Möbius shape of molecular orbitals.


Biosketches

**Dr. Juraj Malinčík** (left) comes from Prievidza, a small town in Slovakia. He graduated at the University of Chemistry and Technology in Prague as a Master of Science in Organic Chemistry (2018). There, he worked in the Svoboda-Kohout research group on photoswitchable liquid crystals. He then moved to the University of Basel where he obtained his Ph.D. in early 2023 under the co-tutorship of Dr. Tomáš Šolomek and Prof. Marcel Mayor exploring new topologies of carbon nanohoops. Currently, he is a postdoctoral fellow in the Šolomek group at the Van’t Hoff Institute for Molecular Sciences (HIMS) at the University of Amsterdam (UvA).

**Dr. Tomáš Šolomek** (right) comes from Prievidza in Slovakia. He obtained his Ph.D. in 2014 jointly at Masaryk University and the University of Fribourg with Prof. Petr Klán and late Prof. Thomas Bally. He was a post-doctoral fellow with Dr. Michal Juríček at the University of Basel and at Northwestern University with Prof. Michael Wasielewski. He launched his independent research at the University of Basel as an Ambizione fellow of the Swiss National Science Foundation. In 2021, he became Assistant Professor at the University of Bern supported by the ERC Starting grant. From 2023, he is a tenure-track Assistant Professor at Van’t Hoff Institute for Molecular Sciences at the University of Amsterdam. His research interests span physical-organic chemistry and organic photochemistry of unusual molecules and reactive intermediates.

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