
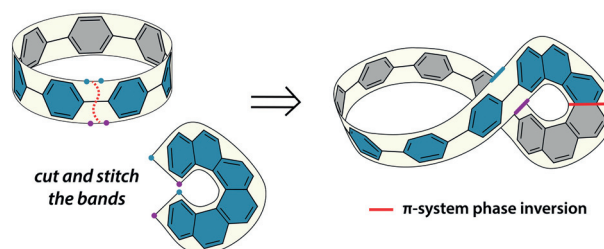


Topological Bistability of the π -System in a Helicene Carbon Nanohoop

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Abstract Molecules with a π -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]cycloparaphenylene, and synthesized the first helicene *para*-phenylene ([6,7]HPP) carbon nanohoop. We have demonstrated that this design strategy ultimately provides a 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 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 left- and right-handedness of the emitted light, each emanating from a conformer with a different π -system topology. Therefore, [6,7]HPP provided the first experimental evidence of such topological bistability in carbon nanohoos.

Key words circularly polarized luminescence, Möbius aromaticity, molecular topology, carbon nanohoos, cycloparaphenylenes, helicenes



Dr. Juraj Malinčík (left) comes from Prievidza, a small town in Slovakia. He graduated from the University of Chemistry and Technology in Prague with a Master of Science degree in organic chemistry (2018). There, he worked in the Svoboda-Kohout research group on photo-switchable 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 Professor Marcel Mayor, exploring new topologies of carbon nanohoos. Currently, he is a postdoctoral fellow in the Šolomek group at the Van 't Hoff Institute for Molecular Sciences at the University of Amsterdam.

Dr. Tomáš Šolomek (right) also comes from Prievidza in Slovakia. He obtained his Ph.D. in 2014 jointly at Masaryk University and the University of Fribourg with Professor Petr Klán and the late Professor Thomas Bally. He was a postdoctoral fellow with Dr. Michal Juríček at the University of Basel, and at Northwestern University with Professor 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 an assistant professor at the University of Bern, supported by an ERC Starting grant. In 2023, he became a tenure-track assistant professor at the 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.

In 1964, Heilbronner published a seminal paper describing a new type of aromaticity.¹ Using Hückel theory, he predicted that twisting the π -electron system of [*n*]annulenes, with their $4m$ π -electrons, into the shape of a Möbius strip should provide a closed-shell system with no loss of resonance energy. Although Heilbronner avoided labeling such a system as aromatic, his prediction clearly suggested its equivalence to the well-established aromatic molecules that follow the Hückel ($4m + 2$) π -electron rule. This report

sparked immense interest within 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 π -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 cyclacenes,^{5–7} and others^{8,9} were found as minima on their respective potential-energy surfaces, but none of these molecules had been experimentally observed at this date. A cyclononatetraenyl cation was the first species that showed experimental evidence of Möbius aromaticity,^{10,11} 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 and co-workers synthesized the first molecular Möbius strip.¹⁸ Although it represented a major step forward, this molecule possessed no π -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 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 to be 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 co-workers developed a synthetic strategy that permitted the synthesis of the first stable Möbius π -extended [16]annulene derivative **1** (Figure 1).²⁰ The synthetic strategy relied on combining moieties that display two different types of π -electron conjugation: (i) a planar/‘normal’ as seen in benzene, and (ii) a radial/in-plane as seen in carbon nanotubes.⁹ It is the latter that leads to twisting of the π -system and localization of most of the strain (Figure 1a).²¹ Theoretical prediction suggested that bianthraquinodimethane embedded in an oligoene system with (E)- or (Z)-double bonds could provide 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 analysis (Figure 1c).²² Both types of isomers of **1** [i.e., with the twisted (Möbius) and with the non-twisted (Hückel) ‘topologies’] were isolated, permitting a direct comparison of the two. The molecular properties that emerge from aromaticity in Möbius **1** could be observed, supporting the prediction of Heilbronner, 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

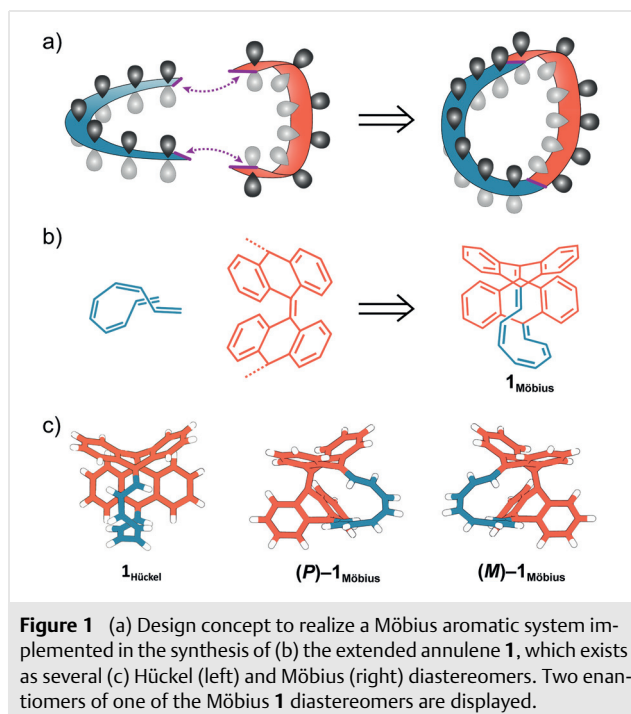
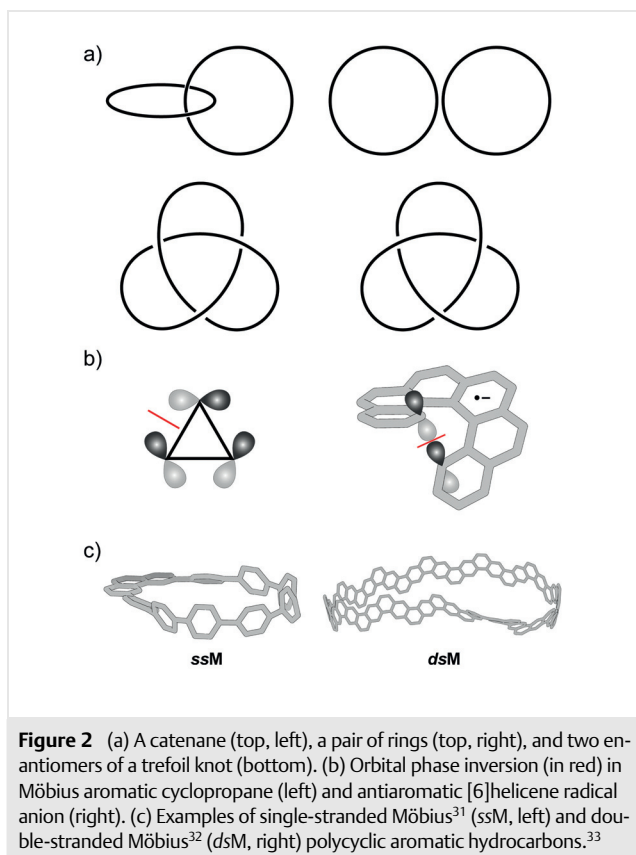


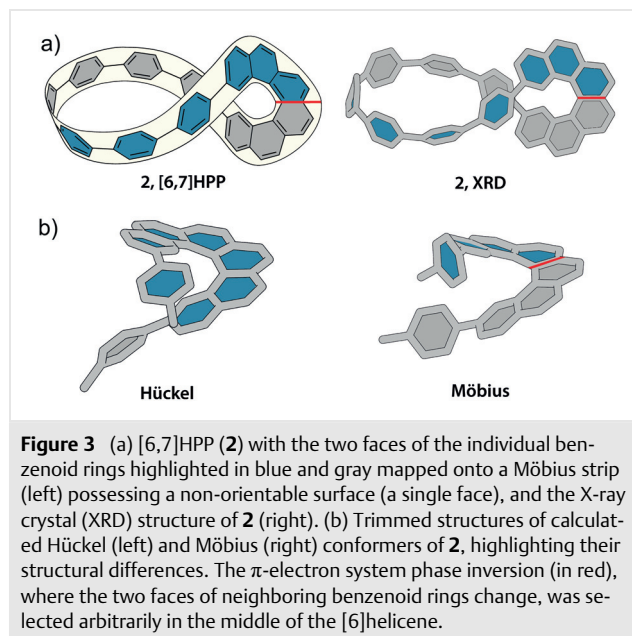
Figure 1 (a) Design concept to realize a Möbius aromatic system implemented in the synthesis of (b) the extended annulene **1**, which exists as several (c) Hückel (left) and Möbius (right) diastereomers. Two enantiomers of one of the Möbius **1** diastereomers are displayed.

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 through 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 labeled 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.⁸ The examples of the in-plane Möbius aromatic cyclopropane³⁰ or Möbius antiaromatic [6]helicene radical anion²⁹ demonstrate this 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).³⁴ 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, whereas the [7]cycloparaphenylene possesses the radial type. Each of these nonplanar moieties helps to distribute the ring strain in the molecule more evenly and permits 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 can be mapped onto a singly twisted Möbius strip (Figure 3a). The presence of the C–C single bonds in **2**, however, permits a relatively rapid rotation of the phenylenes adjacent to the [6]helicene, converting the Möbius conformer into a Hückel conformer ($\Delta G^\circ \approx 5$ 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 here we explicitly distinguish between 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 Möbius molecules’ (ssM) and ‘double-stranded Möbius molecules’ (dsM; Figure 2c), as coined in a recent review by Guo and Stoddart,³⁴ to distinguish the topologically nonequivalent classes of compounds that can, however, both display a non-orientable surface of π -electrons. Thus, both **1** and **2** belong among ssM molecules, whereas Möbius molecular belts^{33,35} are dsM molecules. Clearly, the *topological bistability* of the π -electron system that changes the number of its phase inversions can only be realized in ssM, but not in dsM, molecules.

Similarly, **2** is chiral, and we 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 2.2×10^{-3} . The measured brightness of CPL, $B_{\text{CPL}} = 63$, is relatively high compared with that of other chiral carbon nanostructures^{36–41} and is superior to that of known [6]helicene derivatives.^{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 a 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 π -system in ssM PAHs could permit a more straightforward exploration of the effect of the π -system topology on the mo-

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 ^1H NMR spectroscopy in porphyrinoids^{45–47} but not yet in PAHs.

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

We recorded a series of ^1H 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 closely matched our DFT calculations (~ 8 kcal mol $^{-1}$). 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 ^1H NMR spectrum. Nevertheless, we gathered the first evidence that the two topologies of the π -system lead to an 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_{lum} to that of 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_{lum} , 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_{lum} and the correct energy shift observed in the emission. Note that the short excited-state lifetime does not permit rotation of phenylenes in the excited state, and the steady-state CPL spectrum therefore 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 therefore represents the first example of a PAH for which experimental evidence of the topological bistability of the π -electron system has been collected. Yet, additional model compounds to construct structure–property relationships to strengthen the argument are necessary. Possibly, such compounds might permit the development of a strategy to control the handedness of CPL. Switching of the handedness of the CPL by using external stimuli in polymers,^{48,49} supramolecular assemblies,^{50–56} and liquid crystals⁵⁷ has been 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, whereas a good molecular switch for any practical application in optoelectronic devices should ideally be switchable by a quantitative redox process or by a photon absorption at room temperature.

Others have investigated HPP **2** theoretically for two-photon absorption properties.^{58,59} A few analogous ssM PAHs have appeared in the literature.^{32,60–63} However, the effect of the π -system topology on molecular properties such as (hyper)polarizability has only been studied computationally in these compounds. For example, Liu and Lu investigated different conformations of phenanthroline carbon nanohoops (Figure 2c; left) with different numbers 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*]-cycloparaphenylenes ([*n*]CPPs) themselves require two-electron oxidation to strengthen the π -electron conjugation such that an induced diatropic ring current in [*n*]CPP²⁺ shifts the ^1H 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 and, therefore, an odd number of π -electrons. As a result, **2** is unable to display Möbius (anti)aromaticity, even upon two-electron oxidation, as we confirmed by DFT calculations.³¹

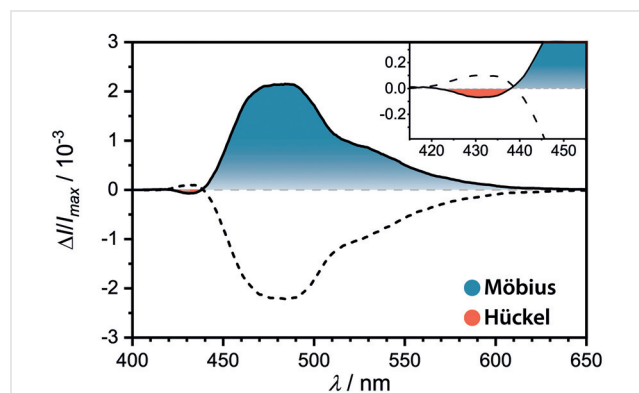


Figure 4 CPL spectra of the enantiomers of **2** with the contributions to the observed luminescence from the individual Hückel and Möbius conformers.

In summary, we hope that we have succeeded in using this Synfact as a platform to clarify the somewhat conflicting language that we found to segue from the topic of aromaticity to molecular nanotopology. The terms that, for historical reasons, are used relatively loosely in the former are regarded with rigor in the latter, which 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 permits a topological bistability of the π -electron system through a simple conformational change. In [6,7]HPP, this leads to a change in 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 from displaying a global (anti)aromaticity, even when oxidized. The reason is that the conjugation path in [6]helicene spans an odd number of carbon atoms. Therefore, we propose to use [5]helicene, which offers conjugation paths with an even number of carbon atoms, and to synthesize members of the [5,*n*]HPP family. These molecules could permit (i) an exploration of 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.

Conflict of Interest

The authors declare no conflict of interest.

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References and Notes

- (1) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923.
- (2) Dobrowolski, J. C. J. *Chem. Inf. Comput. Sci.* **2002**, 42, 490.

- (3) Zoellner, R. W.; Krebs, J. F.; Browne, D. M. *J. Chem. Inf. Comput. Sci.* **1994**, 34, 252.
- (4) Martín-Santamaría, S.; Lavan, B.; Rzepa, H. S. *Chem. Commun.* **2000**, 1089.
- (5) Türker, L. J. *Mol. Struct.: THEOCHEM* **1998**, 454, 83.
- (6) Guillaume, M.; Champagne, B.; Perpète, E. A.; André, J.-M. *Theor. Chem. Acc.* **2001**, 105, 431.
- (7) Martín-Santamaría, S.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2378.
- (8) Rzepa, H. S. *Chem. Rev.* **2005**, 105, 3697.
- (9) Herges, R. *Chem. Rev.* **2006**, 106, 4820.
- (10) Schleyer, P. van. R.; Barborak, J. C.; Su, T. M.; Boche, G.; Schneider, G. *J. Am. Chem. Soc.* **1971**, 93, 279.
- (11) Anastassiou, A. G.; Yakali, E. J. *Chem. Soc., Chem. Commun.* **1972**, 92.
- (12) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. von. R. *Angew. Chem. Int. Ed.* **1998**, 37, 2395.
- (13) Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1996**, 118, 7381.
- (14) Martín-Santamaría, S.; Lavan, B.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1415.
- (15) Havenith, R. W. A.; van Lenthe, J. H.; Jenneskens, L. W. *Int. J. Quantum Chem.* **2001**, 85, 52.
- (16) Castro, C.; Isborn, C. M.; Karney, W. L.; Mauksch, M.; Schleyer, P. von. R. *Org. Lett.* **2002**, 4, 3431.
- (17) Wannere, C. S.; Moran, D.; Allinger, N. L.; Hess, B. A.; Schaad, L. J.; Schleyer, P. von. R. *Org. Lett.* **2003**, 5, 2983.
- (18) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, 104, 3219.
- (19) There are 2250 conceivable *cis/trans* isomers of [16]annulene of which the most stable Möbius one is number 137 in the list of the most stable isomers. See reference 9.
- (20) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, 426, 819.
- (21) Rappaport, S. M.; Rzepa, H. S. *J. Am. Chem. Soc.* **2008**, 130, 7613.
- (22) Ajami, D.; Hess, K.; Köhler, F.; Näther, C.; Oeckler, O.; Simon, A.; Yamamoto, C.; Okamoto, Y.; Herges, R. *Chem. Eur. J.* **2006**, 12, 5434.
- (23) Castro, C.; Chen, Z.; Wannere, C. S.; Jiao, H.; Karney, W. L.; Mauksch, M.; Puchta, R.; van E. Hommes, N. J. R.; von R. Schleyer, P. J. *Am. Chem. Soc.* **2005**, 127, 2425.
- (24) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, 83, 3789.
- (25) Walba, D. M. *Tetrahedron* **1985**, 41, 3161.
- (26) Chambron, J.-C.; Mitchell, D. K. *J. Chem. Educ.* **1995**, 72, 1059.
- (27) Heilbronner 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.
- (28) Although racemization was not experimentally tested.
- (29) Mauksch, M.; Tsogoeva, S. B. *Chem. Eur. J.* **2021**, 27, 14660.
- (30) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, 4, 272.
- (31) Fan, Y.-Y.; Chen, D.; Huang, Z.-A.; Zhu, J.; Tung, C.-H.; Wu, L.-Z.; Cong, H. *Nat. Commun.* **2018**, 9, 3037.
- (32) Segawa, Y.; Watanabe, T.; Yamanoue, K.; Kuwayama, M.; Watanabe, K.; Pirillo, J.; Hijikata, Y.; Itami, K. *Nat. Synth.* **2022**, 1, 535.
- (33) Guo, Q.-H.; Stoddart, J. F. *Chem* **2022**, 8, 2076.
- (34) Malinčík, J.; Gaikwad, S.; Mora-Fuentes, J. P.; Boillat, M.-A.; Prescimone, A.; Häussinger, D.; Campaña, A. G.; Šolomek, T. *Angew. Chem. Int. Ed.* **2022**, 61, e202208591.

- (35) Fan, W.; Fukunaga, T. M.; Wu, S.; Han, Y.; Zhou, Q.; Wang, J.; Li, Z.; Hou, X.; Wei, H.; Ni, Y.; Isobe, H.; Wu, J. *Nat. Synth.* **2023**, *2*, 880.
- (36) Senthilkumar, K.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Cybińska, J.; Zafra, J. L.; Casado, J.; Vives, T.; Crassous, J.; Favereau, L.; Stępień, M. *J. Am. Chem. Soc.* **2019**, *141*, 7421.
- (37) Xu, W.; Yang, X.-D.; Fan, X.-B.; Wang, X.; Tung, C.-H.; Wu, L.-Z.; Cong, H. *Angew. Chem. Int. Ed.* **2019**, *58*, 3943.
- (38) Sato, K.; Hasegawa, M.; Nojima, Y.; Hara, N.; Nishiuchi, T.; Imai, Y.; Mazaki, Y. *Chem. Eur. J.* **2021**, *27*, 1323.
- (39) Nogami, J.; Nagashima, Y.; Miyamoto, K.; Muranaka, A.; Uchiyama, M.; Tanaka, K. *Chem. Sci.* **2021**, *12*, 7858.
- (40) He, J.; Yu, M.-H.; Pang, M.; Fan, Y.-Q.; Lian, Z.; Wang, Y.; Wang, W.-G.; Liu, Y.; Jiang, H. *Chem. Eur. J.* **2022**, *28*, e202103832.
- (41) He, J.; Yu, M.-H.; Lian, Z.; Fan, Y.-Q.; Guo, S.-Z.; Li, X.-N.; Wang, Y.; Wang, W.-G.; Cheng, Z.-Y.; Jiang, H. *Chem. Sci.* **2023**, *14*, 4426.
- (42) Zhao, W.-L.; Li, M.; Lu, H.-Y.; Chen, C.-F. *Chem. Commun.* **2019**, 13793.
- (43) Dhbaibi, K.; Favereau, L.; Srebro-Hooper, M.; Quinton, C.; Vanthuyne, N.; Arrico, L.; Roisnel, T.; Jamoussi, B.; Poriol, C.; Cabanetos, C.; Autschbach, J.; Crassous, J. *Chem. Sci.* **2020**, *11*, 567.
- (44) Dhbaibi, K.; Abella, L.; Meunier-Della-Gatta, S.; Roisnel, T.; Vanthuyne, N.; Jamoussi, B.; Pieters, G.; Racine, B.; Quesnel, E.; Autschbach, J.; Crassous, J.; Favereau, L. *Chem. Sci.* **2021**, *12*, 5522.
- (45) Stępień, M.; Latos-Grażyński, L.; Sprutta, N.; Chwalisz, P.; Szterenber, L. *Angew. Chem. Int. Ed.* **2007**, *46*, 7869.
- (46) Stępień, M.; Sprutta, N.; Latos-Grażyński, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 4288.
- (47) Ghosh, A.; Chaudhary, A.; Srinivasan, A.; Suresh, C. H.; Chandrashekar, T. K. *Chem. Eur. J.* **2016**, *22*, 3942.
- (48) Satrijo, A.; Meskers, S. C. J.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 9030.
- (49) Nishikawa, T.; Nagata, Y.; Suginome, M. *ACS Macro Lett.* **2017**, *6*, 431.
- (50) Gopal, A.; Hifsudheen, M.; Furumi, S.; Takeuchi, M.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 10505.
- (51) Kimoto, T.; Amako, T.; Tajima, N.; Kuroda, R.; Fujiki, M.; Imai, Y. *Asian J. Org. Chem.* **2013**, 404.
- (52) Sun, Z.-B.; Liu, J.-K.; Yuan, D.-F.; Zhao, Z.-H.; Zhu, X.-Z.; Liu, D.-H.; Peng, Q.; Zhao, C.-H. *Angew. Chem. Int. Ed.* **2019**, *58*, 4840.
- (53) Niu, D.; Jiang, Y.; Ji, L.; Ouyang, G.; Liu, M. *Angew. Chem. Int. Ed.* **2019**, *58*, 5946.
- (54) Gao, Y.; Ren, C.; Lin, X.; He, T. *Front. Chem.* **2020**, *8*, 458.
- (55) Jiang, P.; Liu, W.; Li, Y.; Li, B.; Yang, Y. *New J. Chem.* **2021**, *45*, 21941.
- (56) Deng, Y.; Wang, M.; Zhuang, Y.; Liu, S.; Huang, W.; Zhao, Q. *Light: Sci. Appl.* **2021**, *10*, 76.
- (57) Kang, S.; Li, Y.; Bukharina, D.; Kim, M.; Lee, H.; Buxton, M. L.; Han, M. J.; Nepal, D.; Bunning, T. J.; Tsukruk, V. V. *Adv. Mater.* **2021**, *33*, 2103329.
- (58) Li, N.; Sun, M. *ChemPhysChem* **2023**, *24*, e202200846.
- (59) Liu, H.; Li, N.; Xia, J.; Sun, M.; Xia, L. *Chem. Phys. Lett.* **2023**, *826*, 140643.
- (60) Nishigaki, S.; Shibata, Y.; Nakajima, A.; Okajima, H.; Masumoto, Y.; Osawa, T.; Muranaka, A.; Sugiyama, H.; Horikawa, A.; Uekusa, H.; Koshino, H.; Uchiyama, M.; Sakamoto, A.; Tanaka, K. *J. Am. Chem. Soc.* **2019**, *141*, 14955.
- (61) Qiu, Z.-L.; Chen, D.; Deng, Z.; Chu, K.-S.; Tan, Y.-Z.; Zhu, J. *Sci. China Chem.* **2021**, *64*, 1004.
- (62) Li, K.; Xu, Z.; Xu, J.; Weng, T.; Chen, X.; Sato, S.; Wu, J.; Sun, Z. *J. Am. Chem. Soc.* **2021**, *143*, 20419.
- (63) Terabayashi, T.; Kayahara, E.; Zhang, Y.; Mizuhata, Y.; Tokitoh, N.; Nishinaga, T.; Kato, T.; Yamago, S. *Angew. Chem. Int. Ed.* **2023**, *62*, e202214960.
- (64) Liu, Z.; Lu, T. *J. Phys. Chem. C* **2020**, *124*, 7353.
- (65) Toriumi, N.; Muranaka, A.; Kayahara, E.; Yamago, S.; Uchiyama, M. *J. Am. Chem. Soc.* **2015**, *137*, 82.
- (66) Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S. *J. Am. Chem. Soc.* **2016**, *138*, 338.