Möbius Aromaticity

Oct. 18, 2011
M1 Kumiko Yamamoto

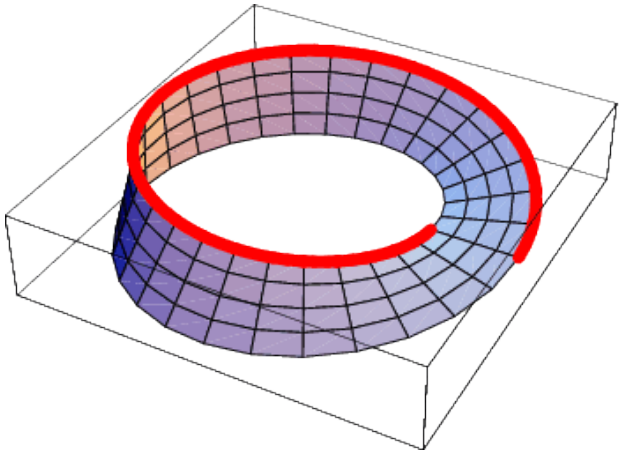
Contents

Möbius Strip

A nonorientable (one-sided) surface obtained by cutting a closed band or cylinder into a single strip, giving one of the two ends thus produced a one-half (180˚) twist, and then reattaching the two ends.

August Ferdinand Möbius (1790-1866)

Johann Benedict Listing (1808-1882)

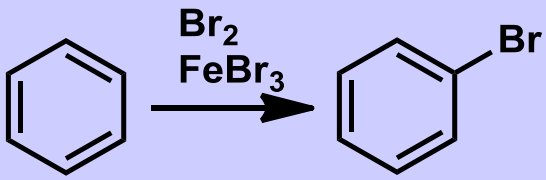


http://mathworld.wolfram.com/MoebiusStrip.html

Criteria of Aromaticity (1)

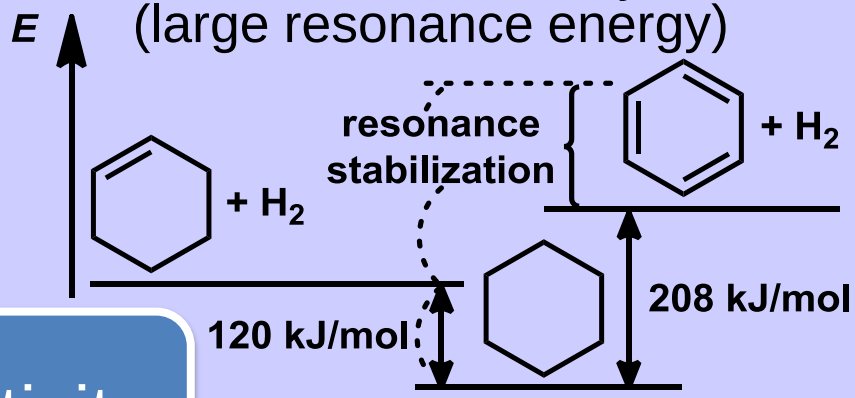
Chemical behavior

electrophilic aromatic substitution



Energetic

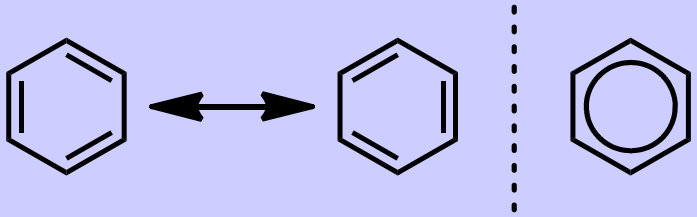
enhanced stability
(large resonance energy)



Aromaticity

Structural

bond length equalization
due to cyclic delocalization



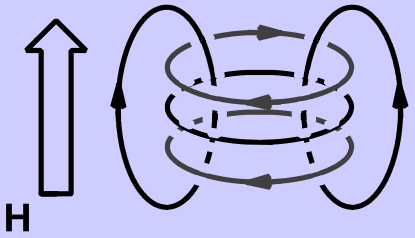
Magnetic

ring current effects

^{1}H NMR chemical shifts

diamagnetic susceptibility exaltation (Λ)

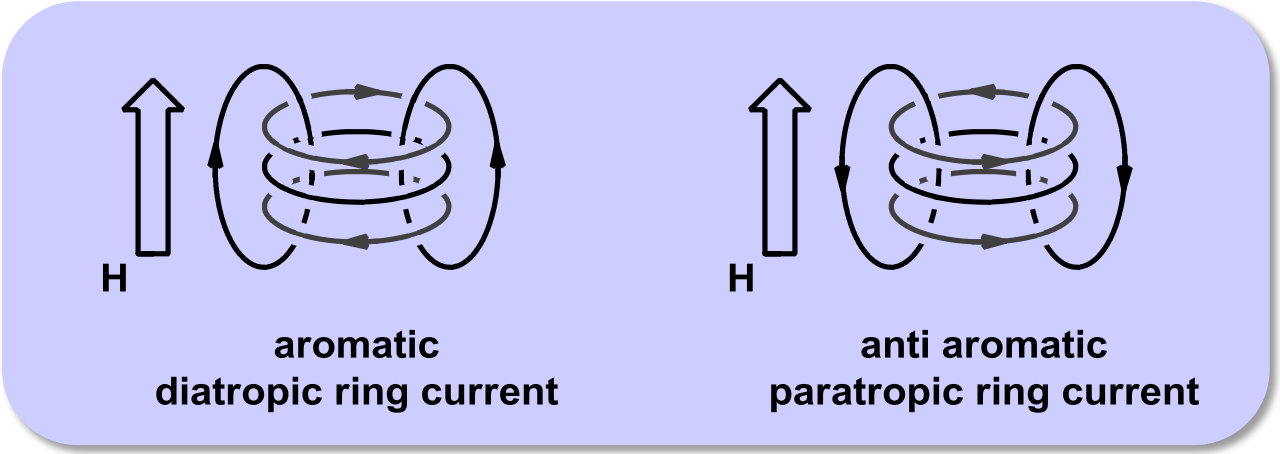
NICS

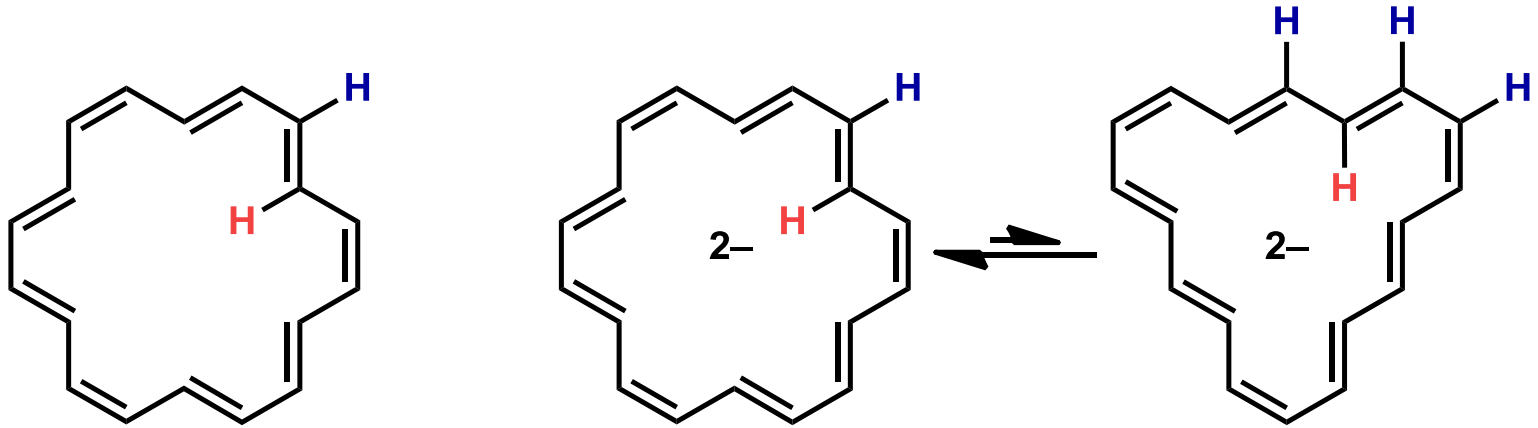


P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209.

Criteria of Aromaticity (2)

Magnetic ^{1}H NMR chemical shifts





9.28 ppm (outer protons)
–2.99 ppm (inner protons)
[18]annulene

–1.13 ppm (outer protons)
29.5 ppm, 28.1 ppm (inner protons)
dianion of [18]annulene

J. F. M. Oth, E. P. Woo, F. Sondheimer, *J. Am. Chem. Soc.* **1973**, *95*, 7337.

Criteria of Aromaticity (3)

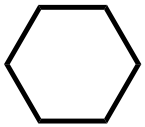
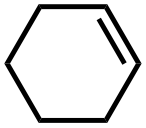
Magnetic diamagnetic susceptibility exaltation (Λ)

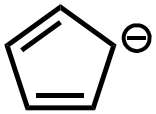
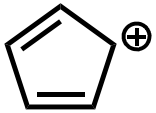
$\Lambda = \chi_M - \chi_{M'}$

- $\Lambda < 0$: **aromatic compounds**
- $\Lambda \sim 0$: **nonaromatic compounds**

χ_M: **the experimentally determined molar susceptibility of a compound**

$\chi_{M'}$: **the susceptibility estimated for a cyclopolyene of that structure**

Compound	χ_M	$\chi_{M'}$	Λ
	−68.1	−68.1	0.0
	−57.5	−58.3	0.8
	−48.6	−49.3	0.7
	−54.8	−41.1	−13.7

Compound	χ_M	$\chi_{M'}$	Λ
	-	-	−17.2**
	−44.5	−38.0	−6.5 (−2.4**)
	-	-	32.6**

*All values of χ_M, $\chi_{M'}$, and Λ are given in units of 10^{-6} cm^3 mol^{-1} (ppm·cgs). **The calculated magnetic susceptibility exaltations.

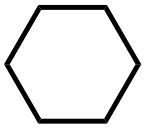
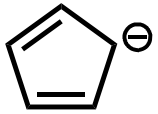
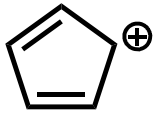
H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, *J. Am. Chem. Soc.* **1968**, *90*, 811.

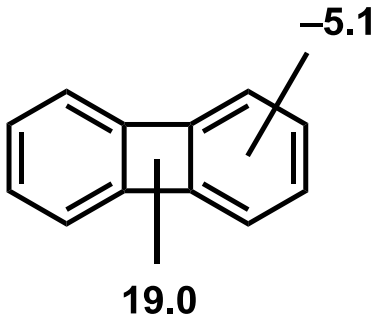
H. J. Dauben, Jr., J. D. Wilson, J. L. Laity, *J. Am. Chem. Soc.* **1969**, *91*, 1991.

Criteria of Aromaticity (4)

Magnetic NICS (nucleus-independent chemical shift)

absolute magnetic shieldings, computed at ring centers
- **NICS < 0 : aromaticity**
- **NICS > 0 : antiaromaticity**

Compound	Λ	NICS	Compound	Λ	NICS
	0.0	−2.2		−17.2**	−14.3
	−13.7	−9.7		−6.5 (−2.4**)	−3.2
				32.6**	54.2

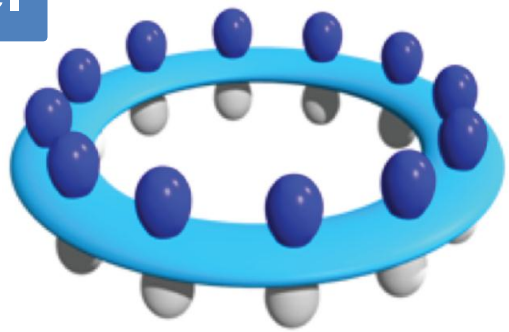


*All values of Λ are given in units of 10^{-6} cm^3 mol^{-1} (ppm·cgs) and NICS are given in units of ppm. **The calculated magnetic susceptibility exaltations.

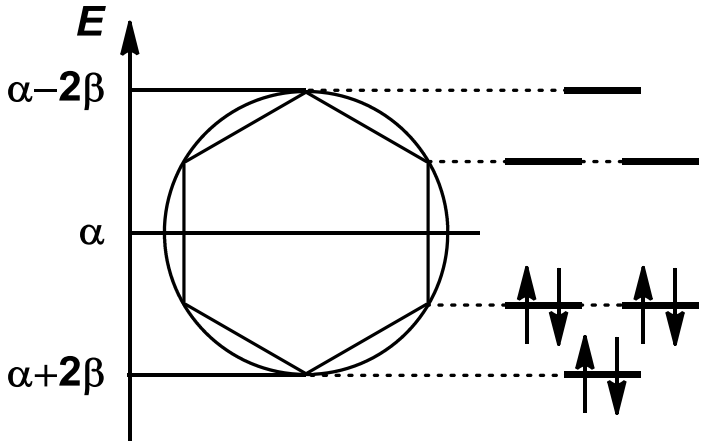
P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

Implications of Möbius Aromaticity

Hückel



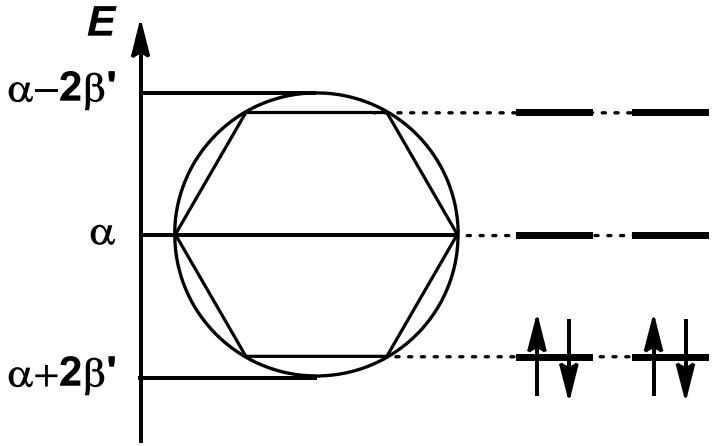
$(4n+2)\pi$: aromatic
$4n\pi$: antiaromatic



$$\varepsilon_k = \alpha + 2\beta \cos\frac{2k\pi}{N}$$

Möbius

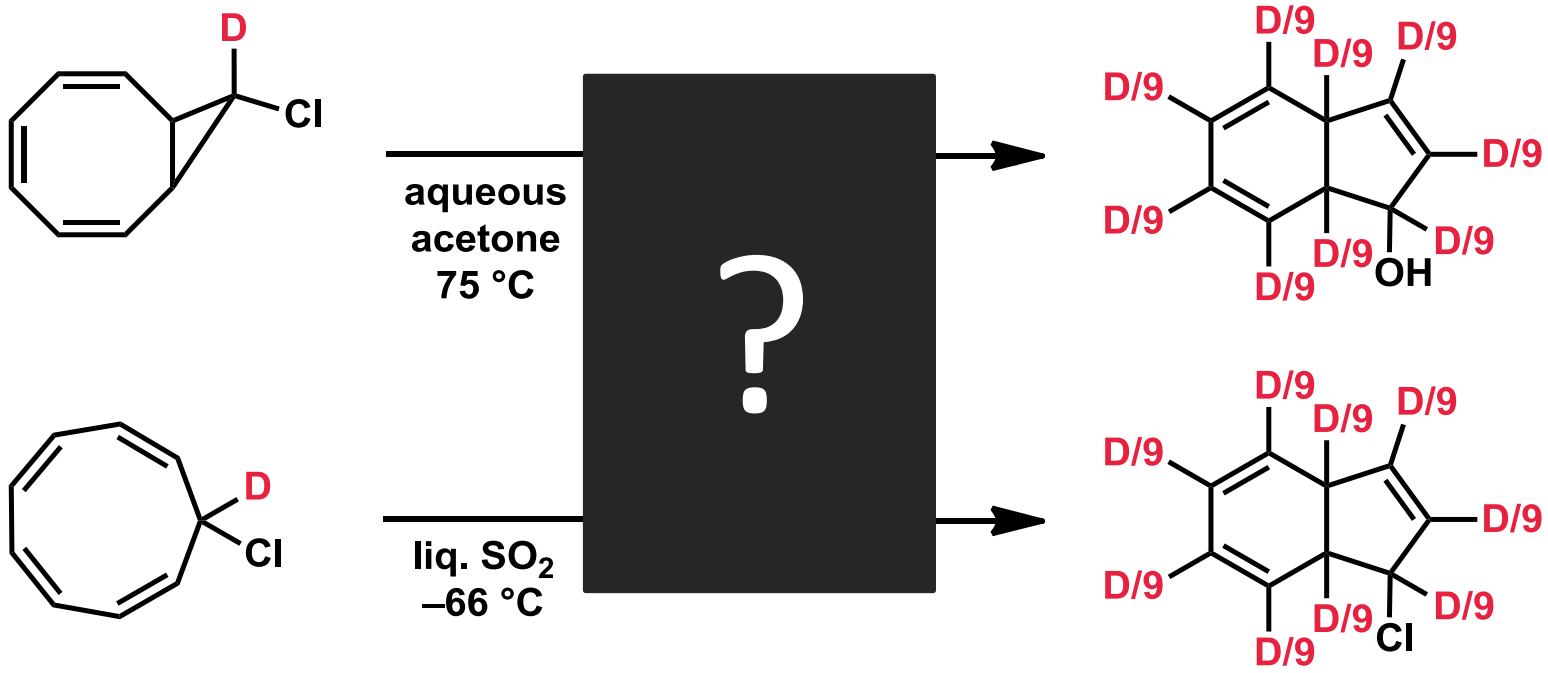
$4n\pi$: aromatic
$(4n+2)\pi$: antiaromatic



$$\varepsilon_k = \alpha + 2\beta' \cos\frac{(2k+1)\pi}{N}$$

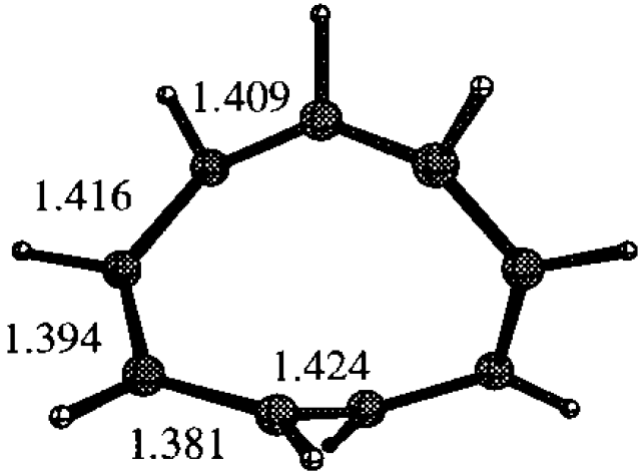
E. Heilbronner, *Tetrahedron Lett.* **1964**, *29*, 1923.

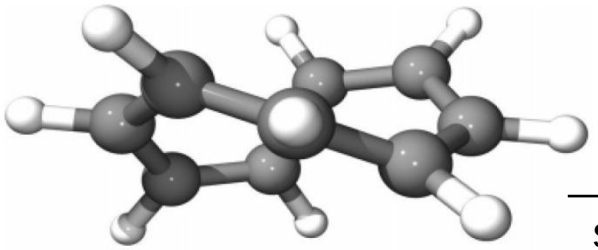
A Cationic Möbius Aromatic System (1)



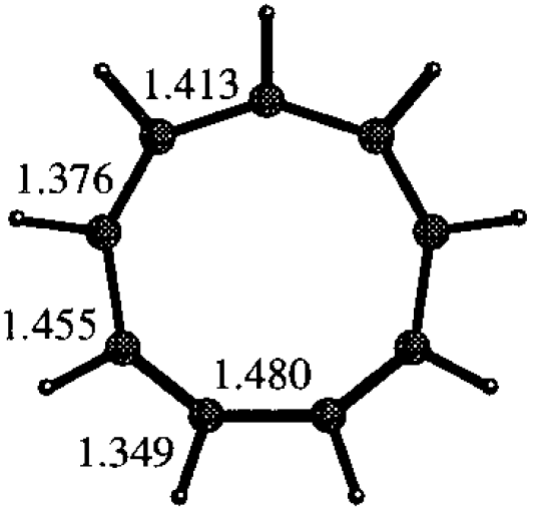
J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, G. Schneider, *J. Am. Chem. Soc.* **1971**, *93*, 279.
A. G. Anastassiou, E. Yakali, *J. Chem. Soc. Chem. Commun.* **1972**, 92.

A Cationic Möbius Aromatic System (2)





C_2



C_{2v}
(planar geometry)

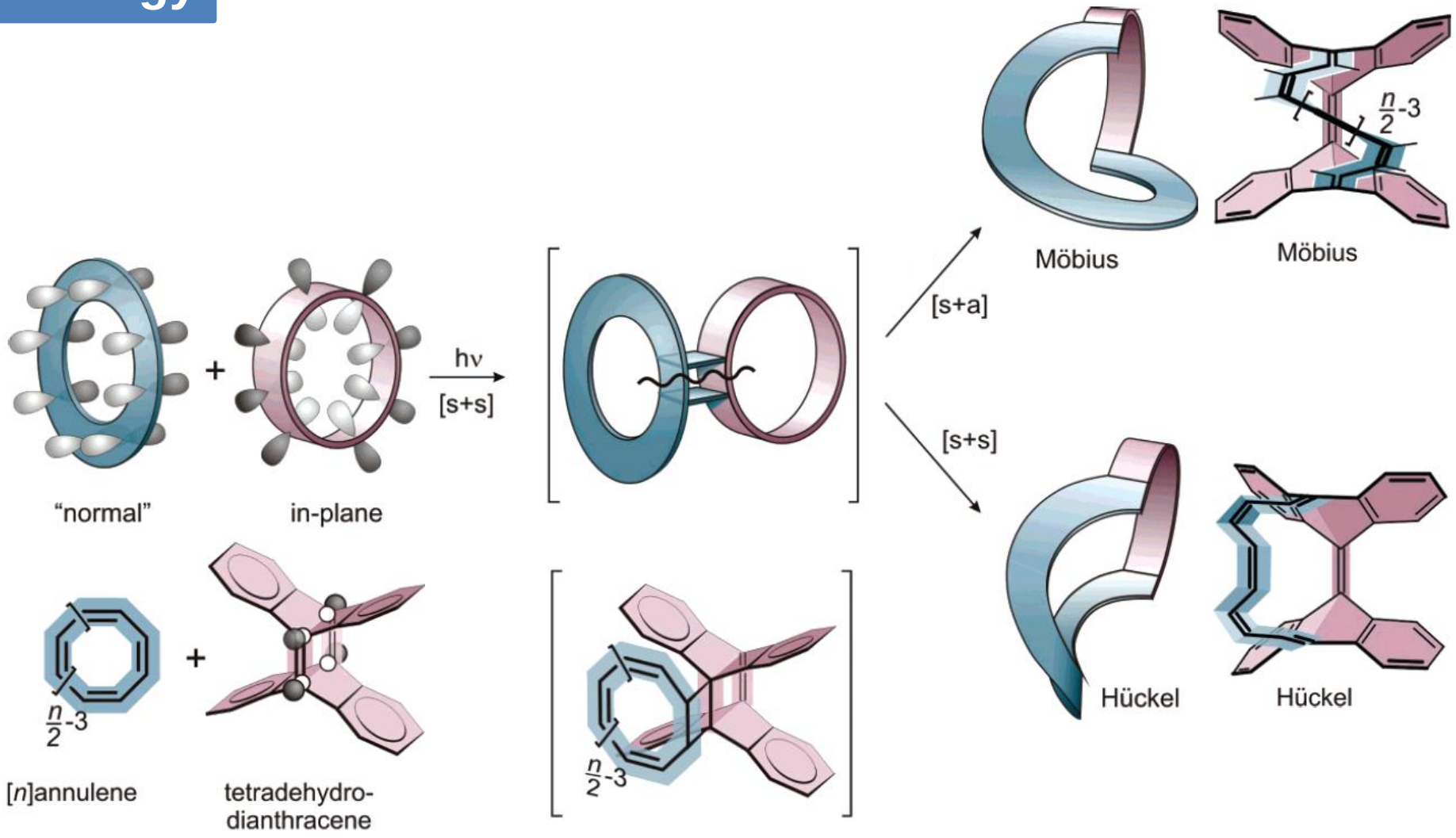
species	E_{rel} (kcal/mol)	ΔR_{C-C} (Å)	Λ (ppm•cgs)	NICS (ppm)
C_2	0.0	0.043	–18.8	–13.4
C_{2v}	+26.3	0.131	+112.2	+42.0

Eight-electron monocyclic cation $(CH)_9^+$ actually does prefer C_2-symmetrical structure and is Möbius aromatic rather than nonaromatic.

M. Mauksch, V. Gogonea, H. Jiao, P. v. R. Schleyer, *Angew. Chem. Int. Ed.* **1998**, *37*, 2395.

Synthesis and Properties of a Möbius Cycloalkene (1)

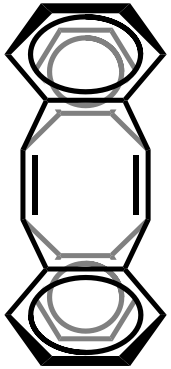
Strategy



D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature*, **2003**, *426*, 819.

Synthesis and Properties of a Möbius Cycloalkene (2)

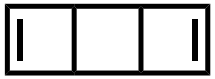
Synthesis



TDDA

II

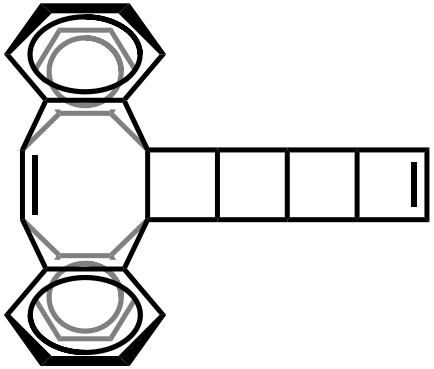
+



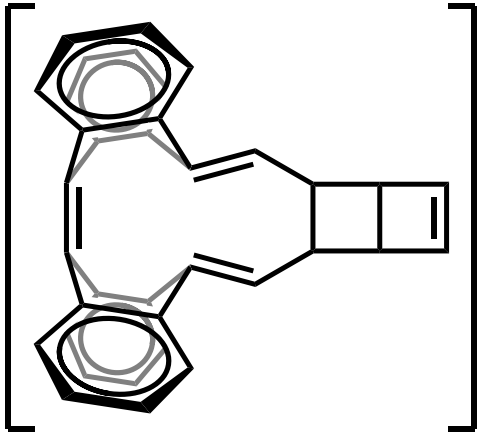
syn-TCOD

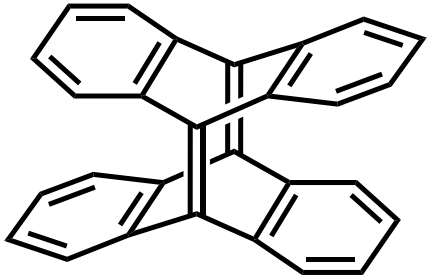
hν

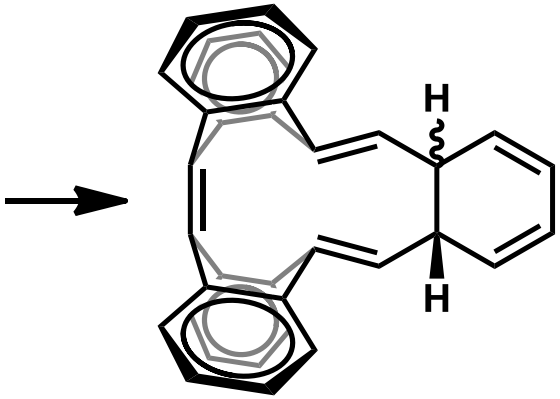
30 min



isolated, NMR





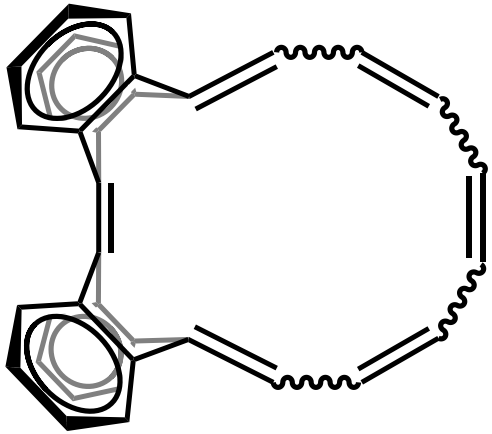


two isomers

hν

254 nm

24 h



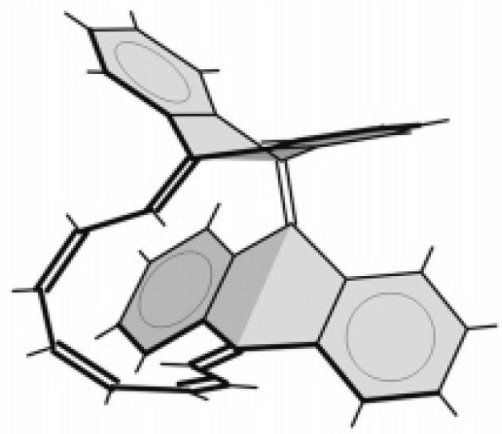
five isomers

ca. 50% yield

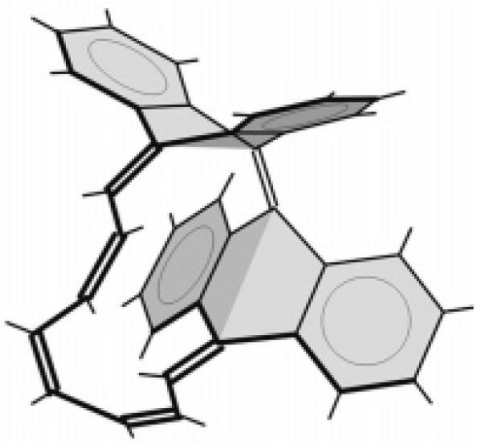
D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature*, **2003**, *426*, 819.

Synthesis and Properties of a Möbius Cycloalkene (3)

Properties



C_2 Möbius



C_S Hückel

species	color	HOMA (polyene bridge)	HOMA (all bonds)	ΔR_{C-C} (Å) (polyene bridge)	$ISE_{Iluncorr}$* (kcal/mol)
C_2 Möbius	red	0.50	0.35	0.095	4.04
C_S Hückel	colorless	0.05	0.17	0.143	–2.22

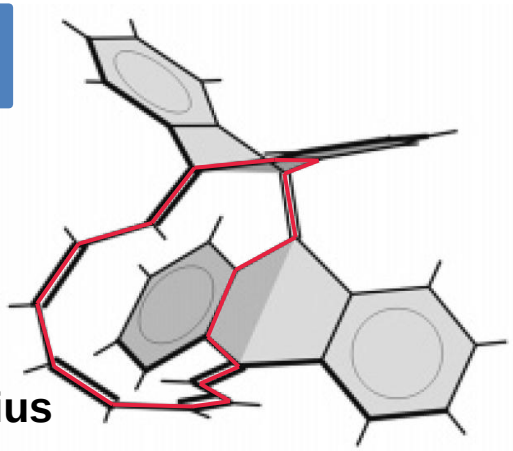
*An aromatic stabilization energy, computed by the indene/isoindene approach.

"Taken together, the observed trends in bond-length equalization and stabilization energy indicate that the Möbius structure is moderately aromatic, whereas the Hückel structure is nonaromatic."

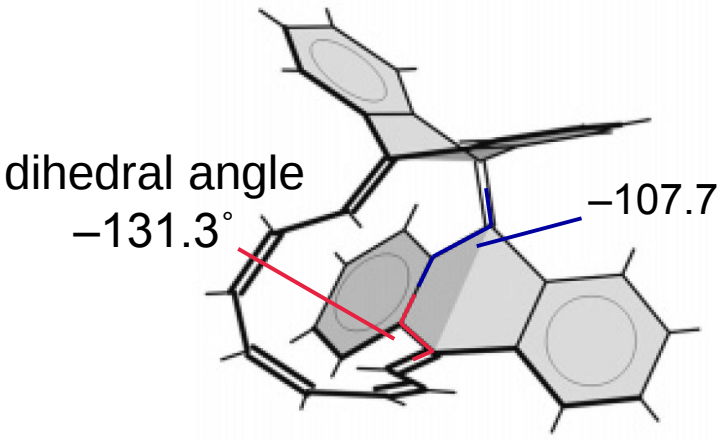
D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature*, **2003**, *426*, 819.

Synthesis and Properties of a Möbius Cycloalkene (4)

Discussion



C_2 **Möbius**



data source	HOMA	ΔR_{C-C} (Å)
Herges et al. *Nature*	0.35 (entire molecule)	0.095 (polyene bridge)
Castro et al. *J. Am. Chem. Soc.*	–0.02 ([16]annulene core)	0.135 ([16]annulene core)

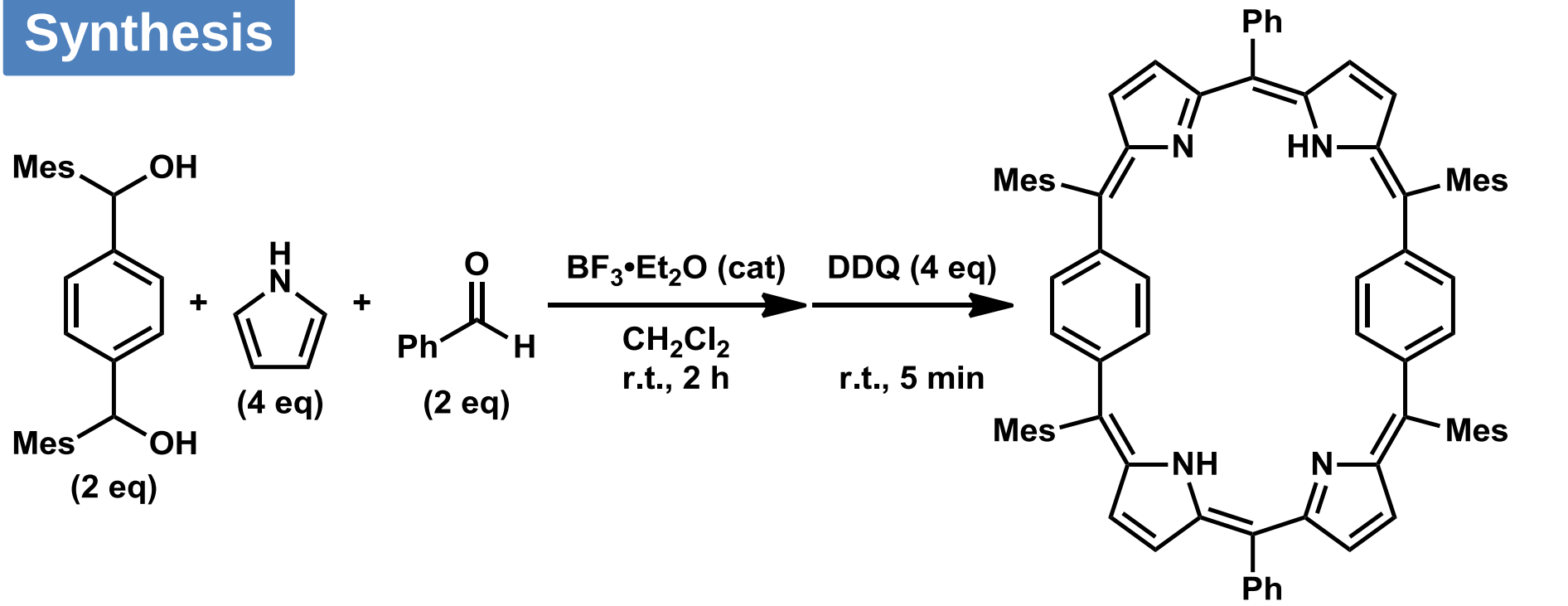
"we conclude that the [16]annulene core of 1 is nonaromatic and that any aromatic character of 1 is confined to the benzene rings." (**1** = C_2 Möbius)

ISE_{II} (kcal/mol)	NICS (ppm)	Λ (ppm•cgs)
4.04 (uncorrected)	-	-
0.6 (corrected)	–3.4	–30.0 (uncorrected) +19.6 (corrected)

C. Castro, Z. Chen, C. S. Wannere, H. Jial, W. L. Karney, M, Mauksch, R. Puchta, N. J. R. v. E. Hommes, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2005**, *127*, 2425.

Expanded Porphyrin with a Hückel-Möbius Topology Switch (1)

Synthesis

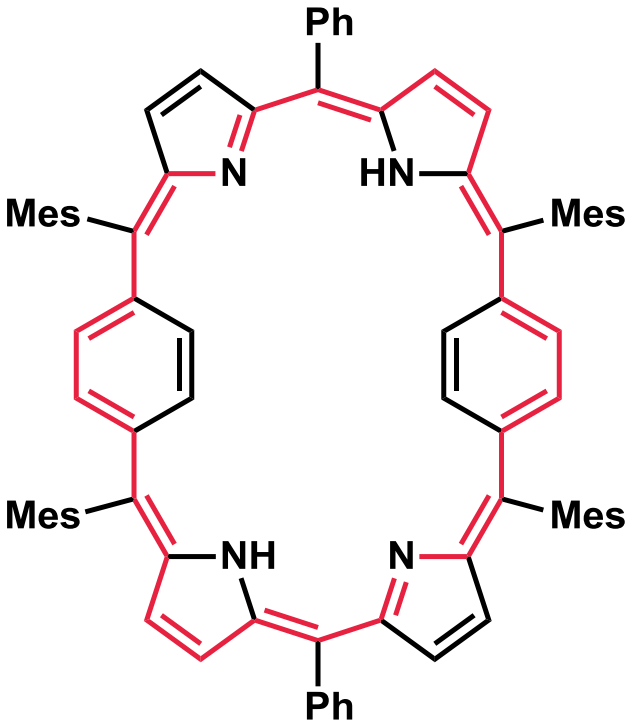


A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1)
5% yield

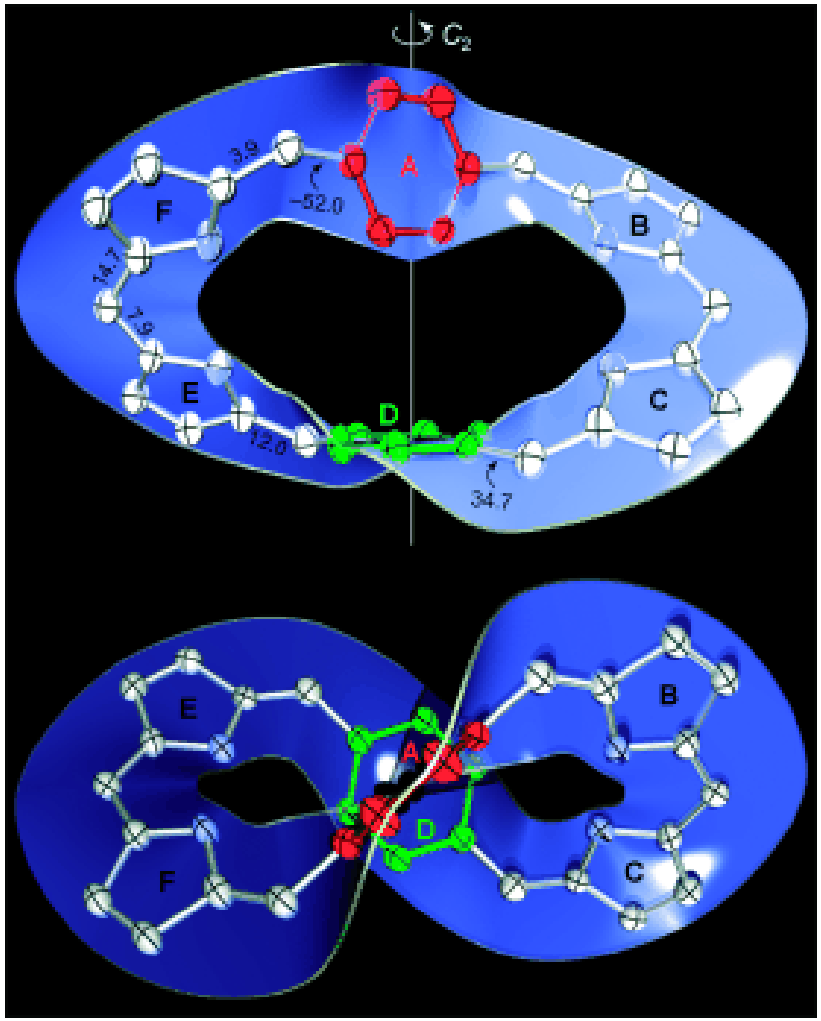
M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem. Int. Ed.* **2007**, *46*, 7869.

Expanded Porphyrin with a Hückel-Möbius Topology Switch (2)

Properties X-ray crystal structure



A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1)
28π electron pathway

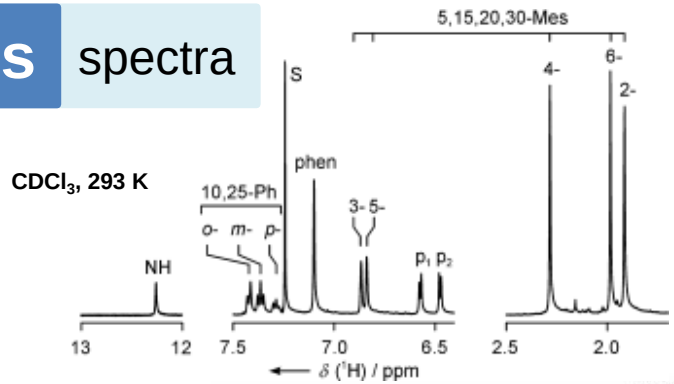


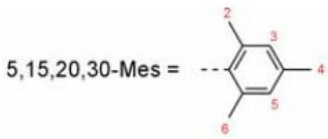
X-ray crystal structure of A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1).

M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem. Int. Ed.* **2007**, *46*, 7869.

Expanded Porphyrin with a Hückel-Möbius Topology Switch (3)

Properties spectra

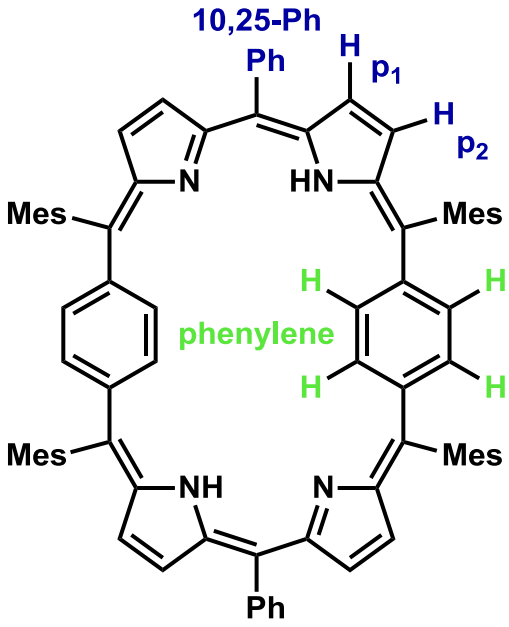


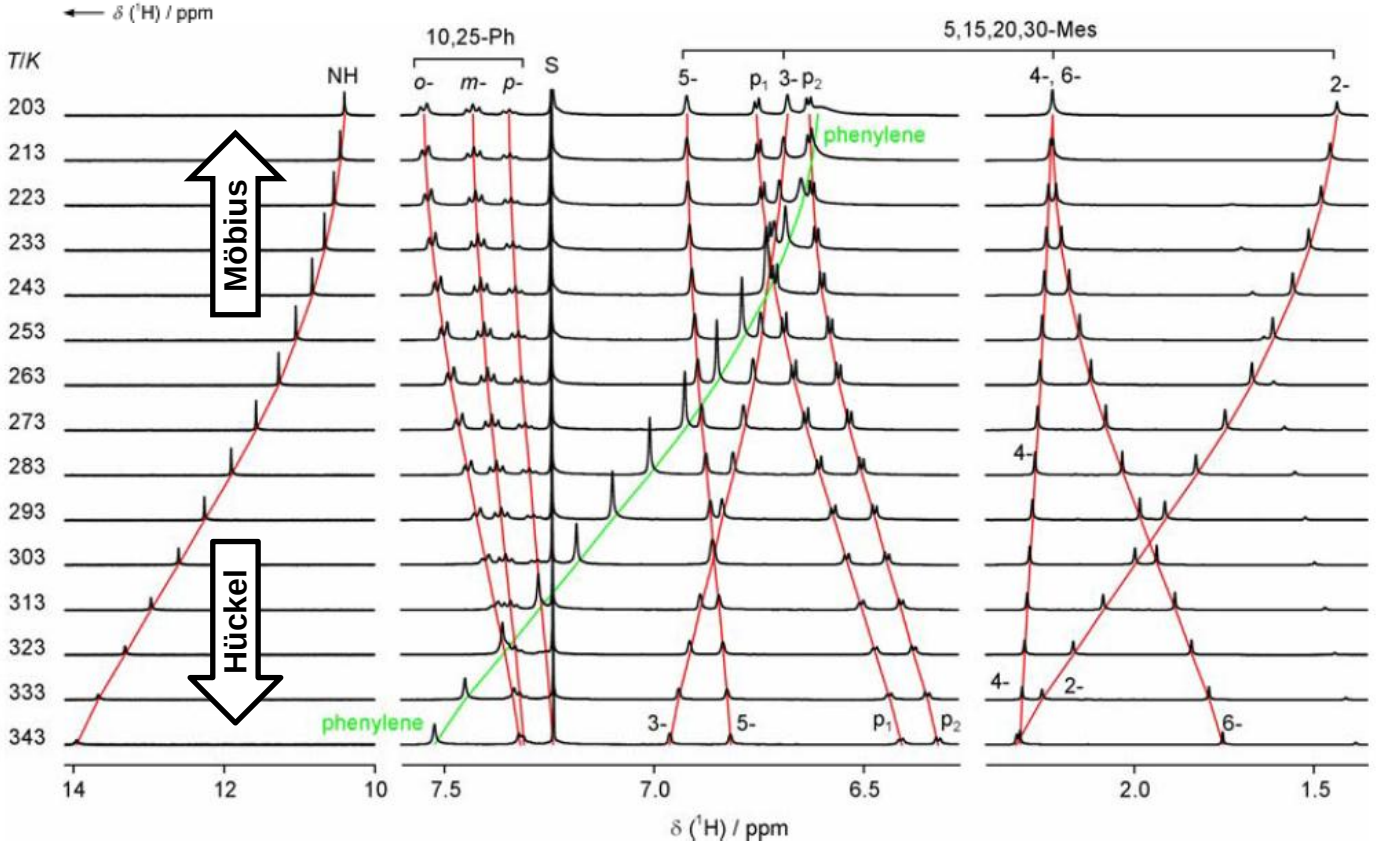


p_1 = 8,12,23,27-H

p_2 = 7,13,22,28-H

phenylene = 2,3,17,18,31,32,35,36-H

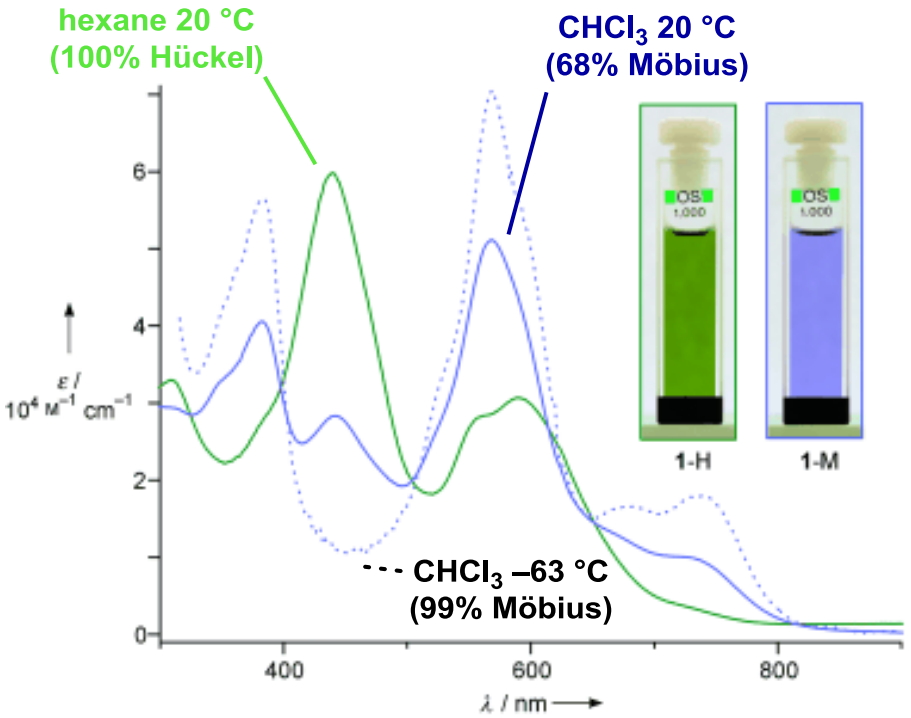




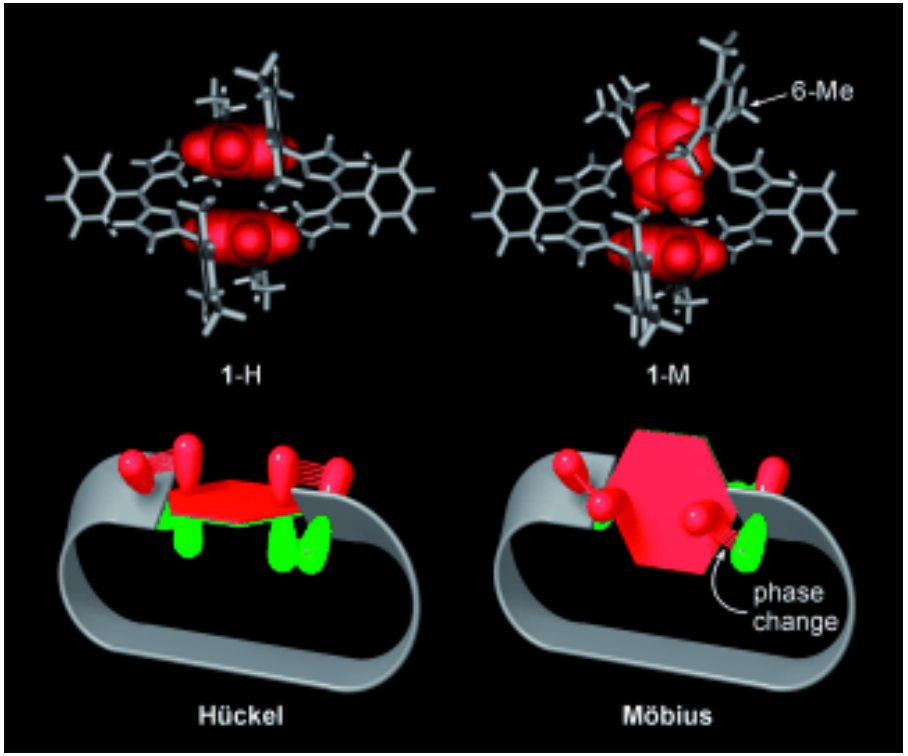
M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem. Int. Ed.* **2007**, *46*, 7869.

Expanded Porphyrin with a Hückel-Möbius Topology Switch (4)

Properties electron-absorption spectra and DFT calculations



Electronic-absorption spectra of A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1).

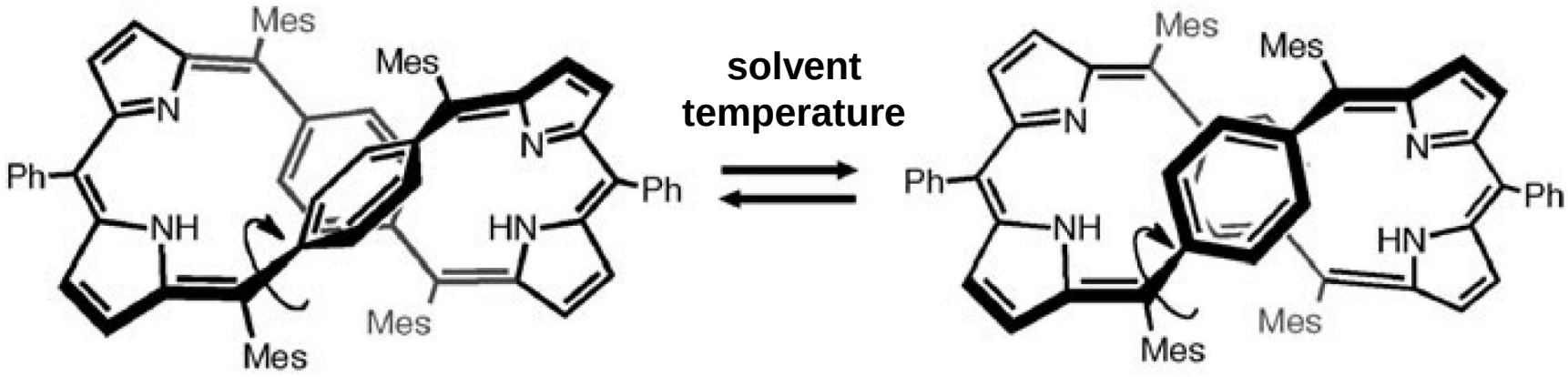


DFT-optimized geometries of the Hückel and Möbius conformers of A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1).

M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg, *Angew. Chem. Int. Ed.* **2007**, *46*, 7869.

Expanded Porphyrin with a Hückel-Möbius Topology Switch (5)

Conclusion



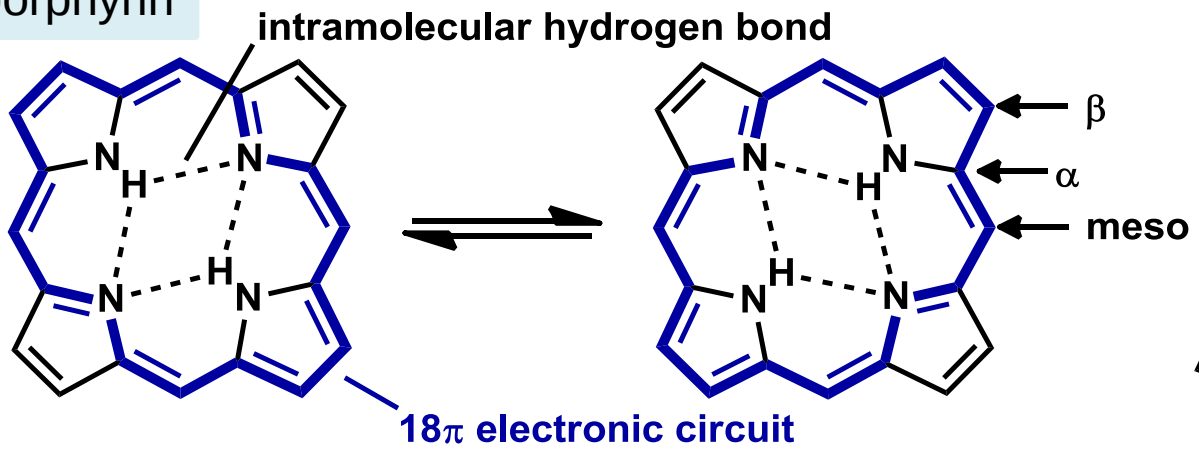
Möbius topology **Hückel topology**

A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1) is the first example of dynamic switching between Hückel and Möbius topologies in a conjugated molecule.

Expanded Porphyrins with a Möbius Aromaticity (1)

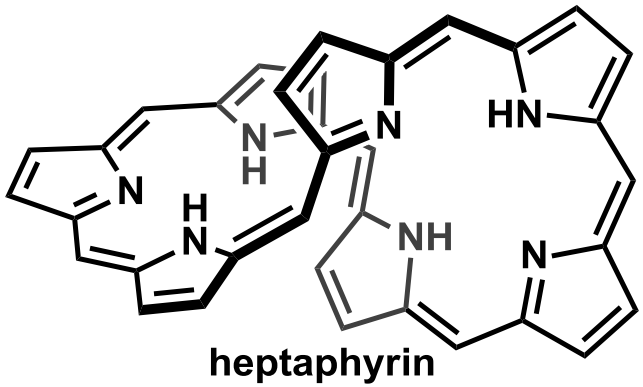
Expanded Porphyrins

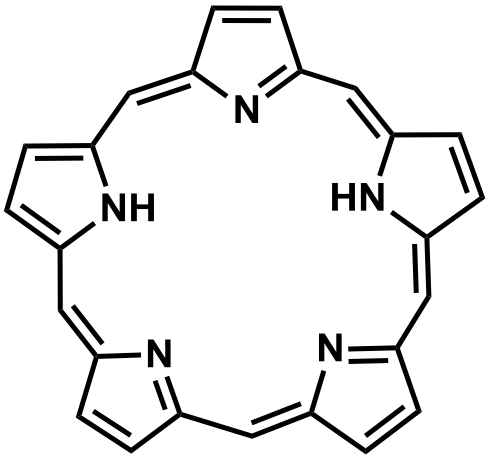
porphyrin

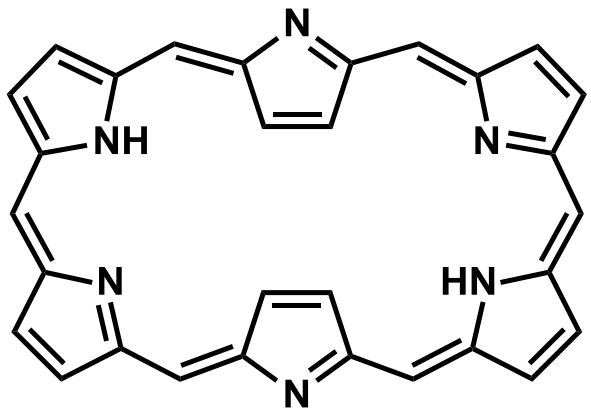


expanded porphyrins

Macrocycles that contain "pyrrole, furan, thiophene, or other heterocyclic subunits linked together either directly or through one or more spacer atoms in such a manner that the internal ring pathway contains a minimum of 17 atoms".


heptaphyrin

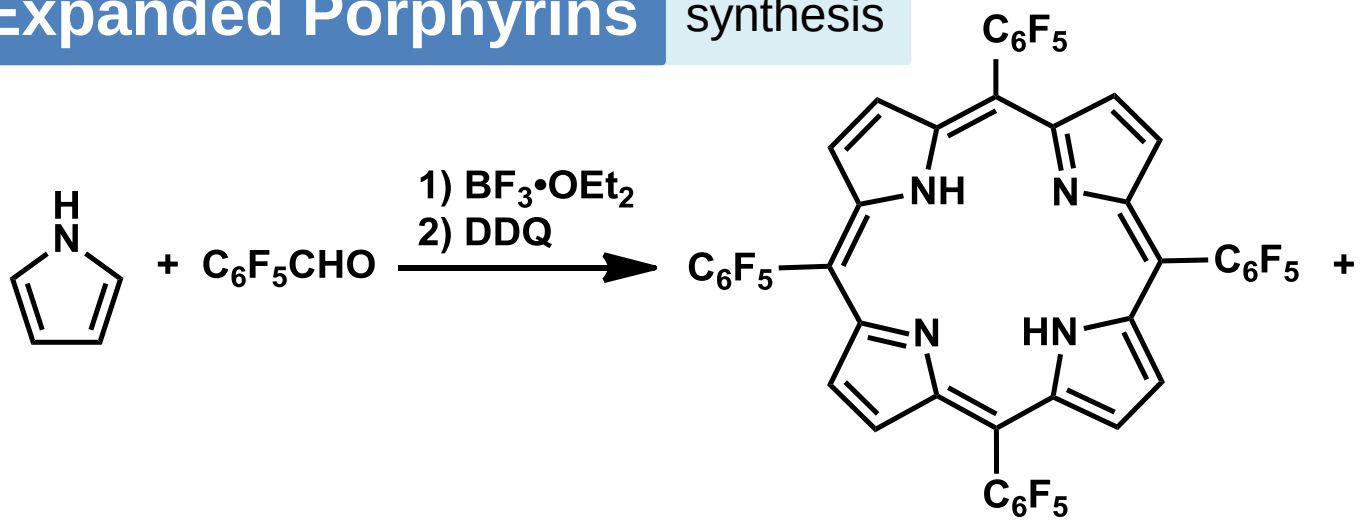

pentaphyrin


hexaphyrin

J. L. Sessler, D. Seidel, *Angew. Chem. Int. Ed.* **2003**, *42*, 5134.

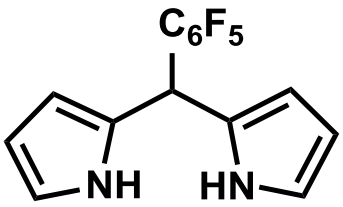
Expanded Porphyrins with a Möbius Aromaticity (2)

Expanded Porphyrins synthesis



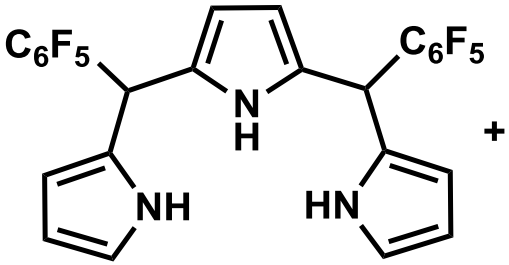
porphyrin, *N* = 4: 11% yield

J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190.



+ C_6F_5CHO → 1) MsOH, 2) DDQ → ***N* = 4, 6, 8, •••**

Y. Tanaka, J.-Y. Shin, A. Osuka, *Eur. J. Org. Chem.* **2008**, 1341.

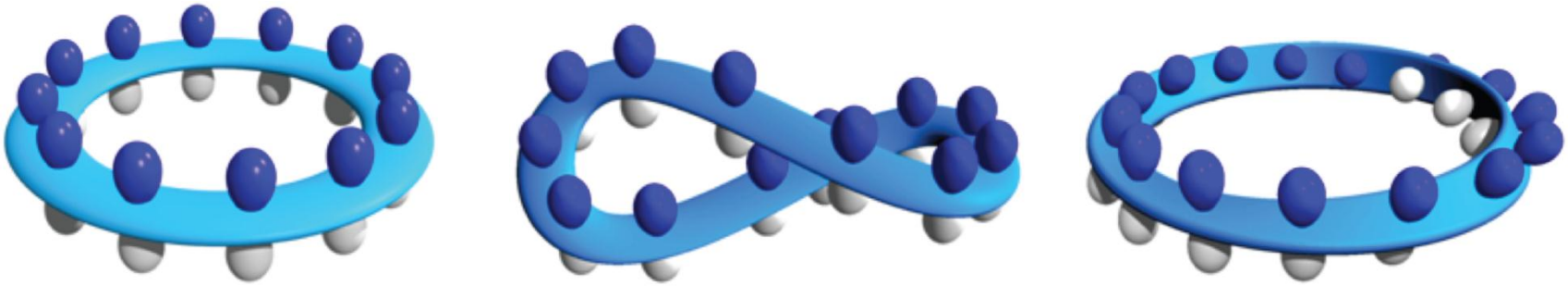


+ C_6F_5CHO → 1) MsOH, 2) DDQ → ***N* = 6, 9, 12, •••**

Y. Kamimura, S. Shimizu, A. Osuka, *Chem. Eur. J.* **2007**, *13*, 1620.

Expanded Porphyrins with a Möbius Aromaticity (3)

Expanded Porphyrins relationship between topology and aromaticity



planar Hückel **figure-eight Hückel** **Möbius**

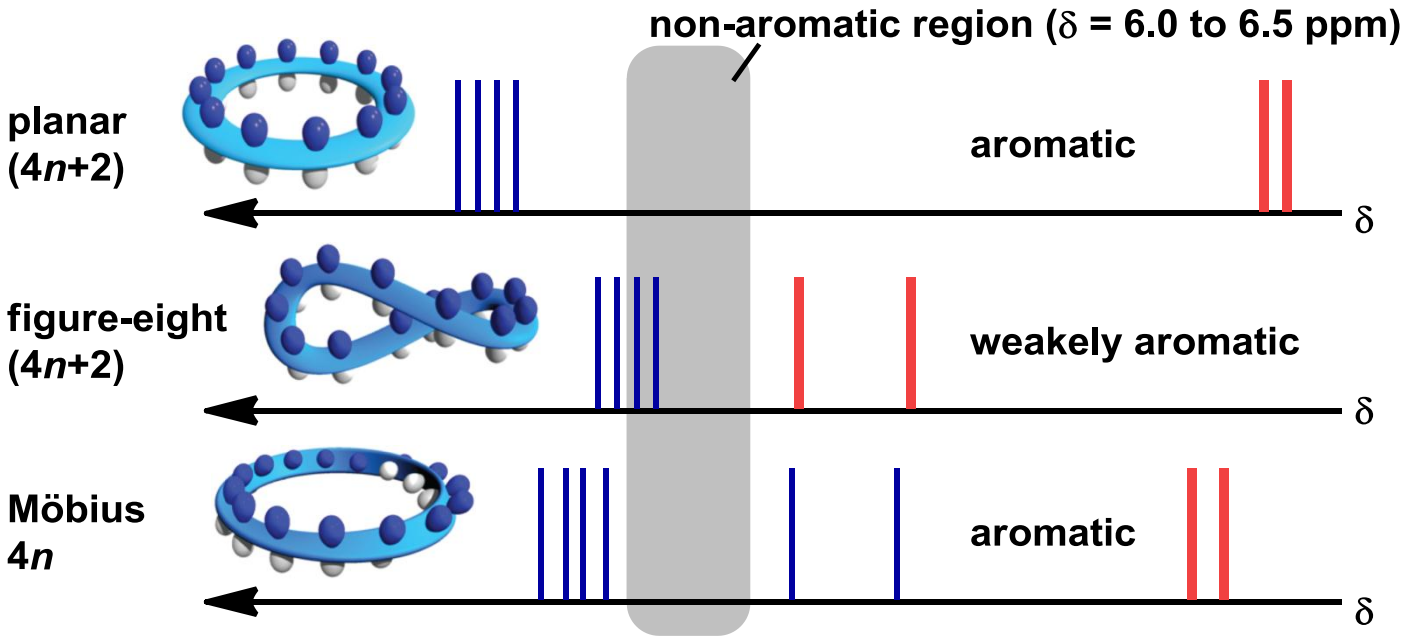
$(4n+2)\pi$ **: aromaticity**
$4n\pi$ **: antiaromaticity**

$4n\pi$ **: aromaticity**
$(4n+2)\pi$ **: antiaromaticity**

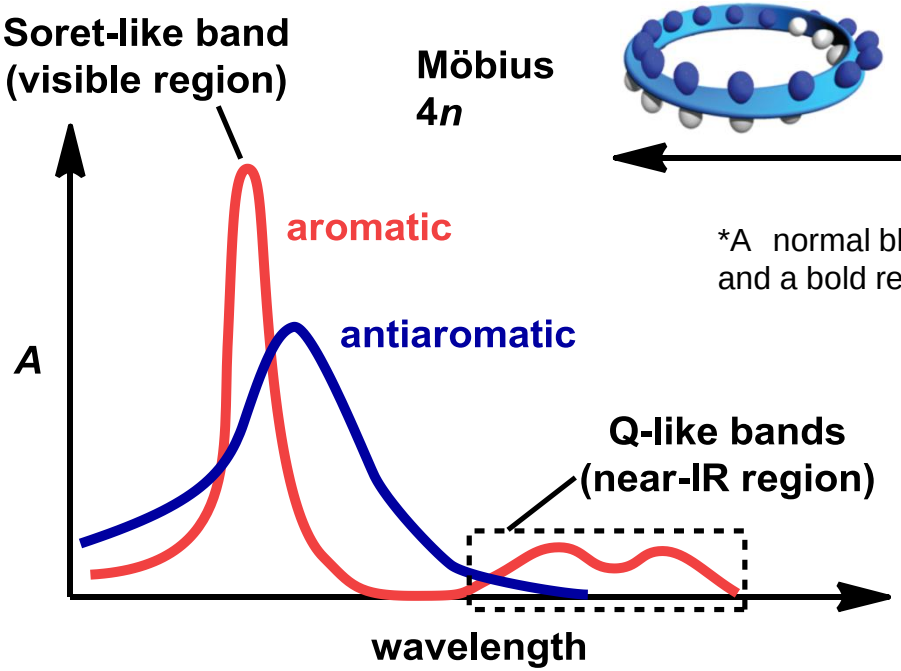
S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2011**, *50*, 4342.

Expanded Porphyrins with a Möbius Aromaticity (4)

Expanded Porphyrins aromaticity of expanded porphyrins



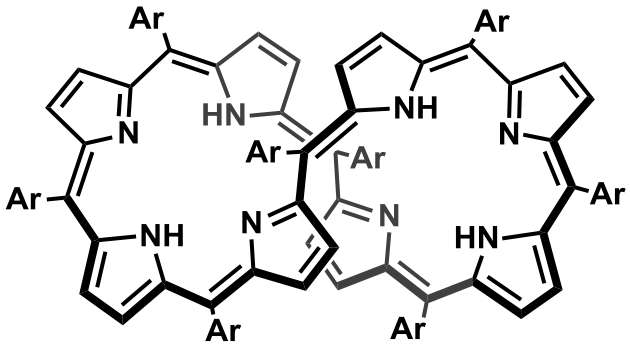
*A normal blue line indicates the signals of the outer pyrrolic β protons and a bold red line indicates those of inner protons.



S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2011**, *50*, 4342.

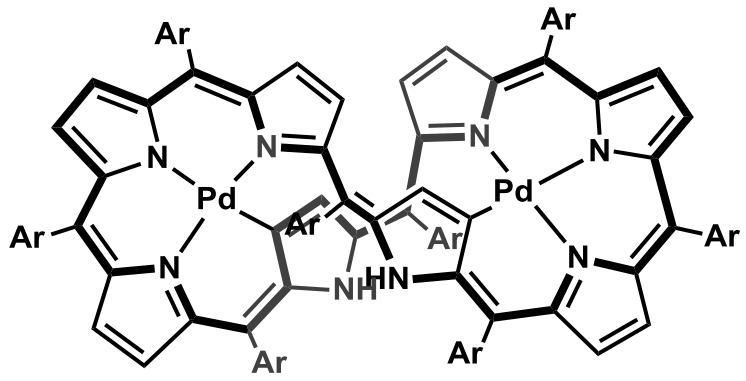
Expanded Porphyrins with a Möbius Aromaticity (5)

Bis-Pd^{II} [36]octaphyrin synthesis



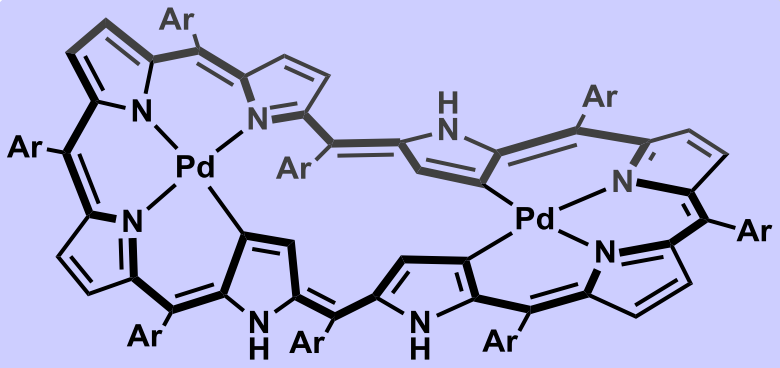
$Pd(OAc)_2$ (10 eq)
NaOAc (10 eq)

MeOH
reflux, 2 h



51% yield

+

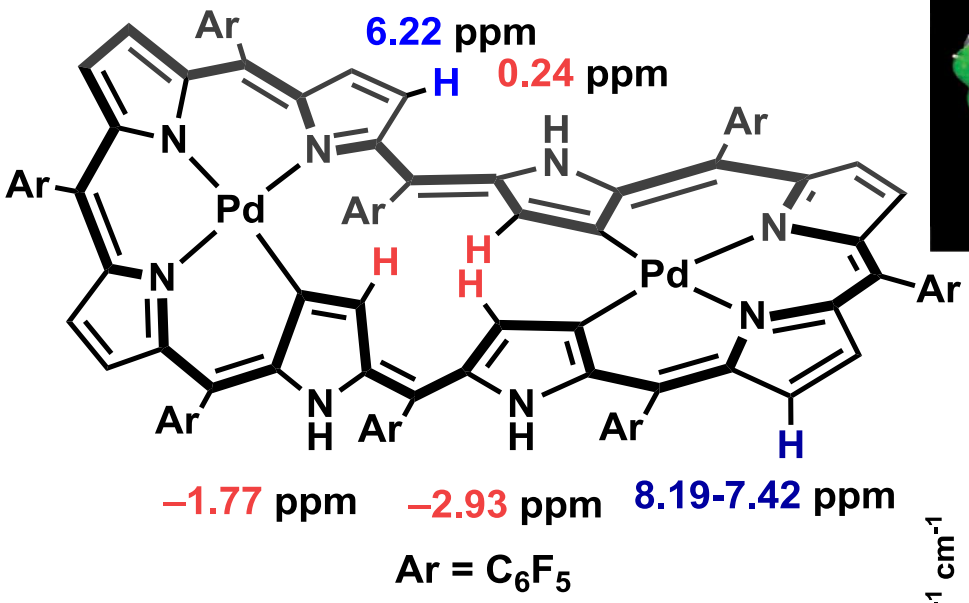


20% yield

Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 681.

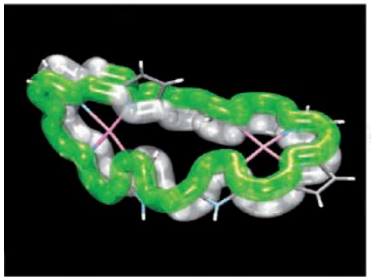
Expanded Porphyrins with a Möbius Aromaticity (6)

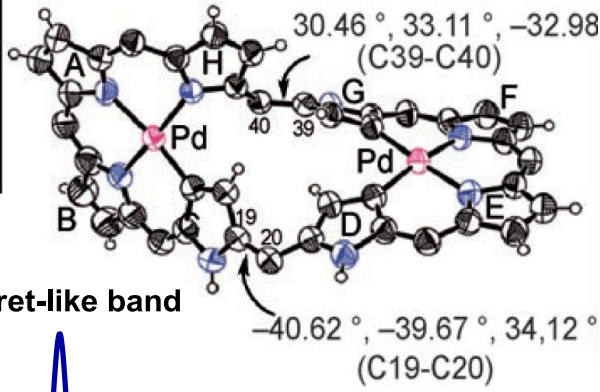
Bis-Pd^{II} [36]octaphyrin properties

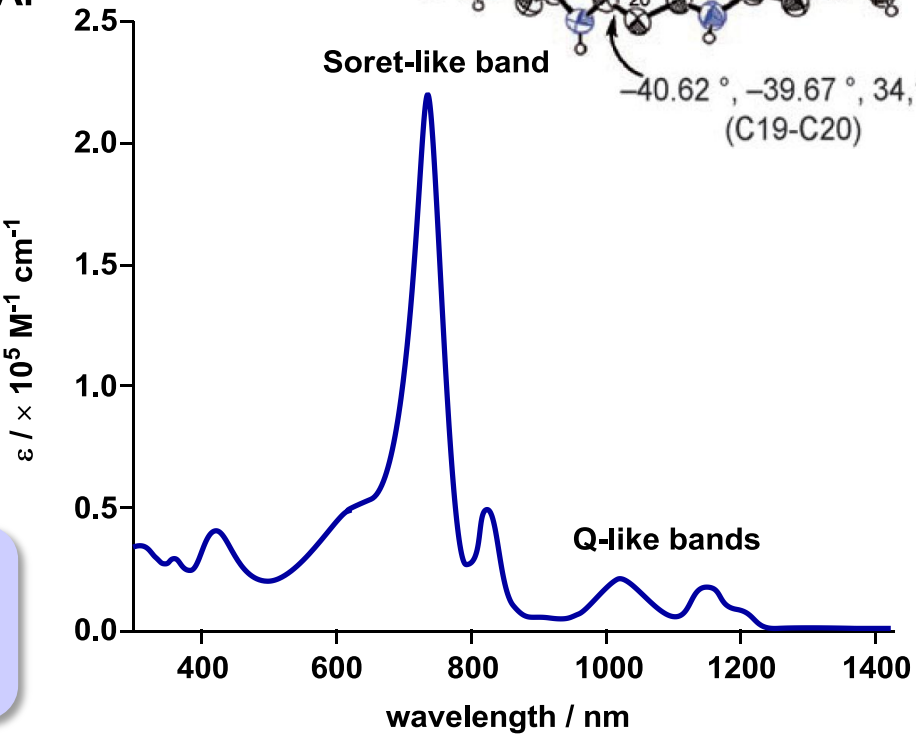


ΔR_{C-C} (Å)	NICS (ppm)	HOMA
0.113	–14.6	0.67

"metal complex is stable, conformationally locked Möbius aromatic molecule that displays distinct aromaticity."





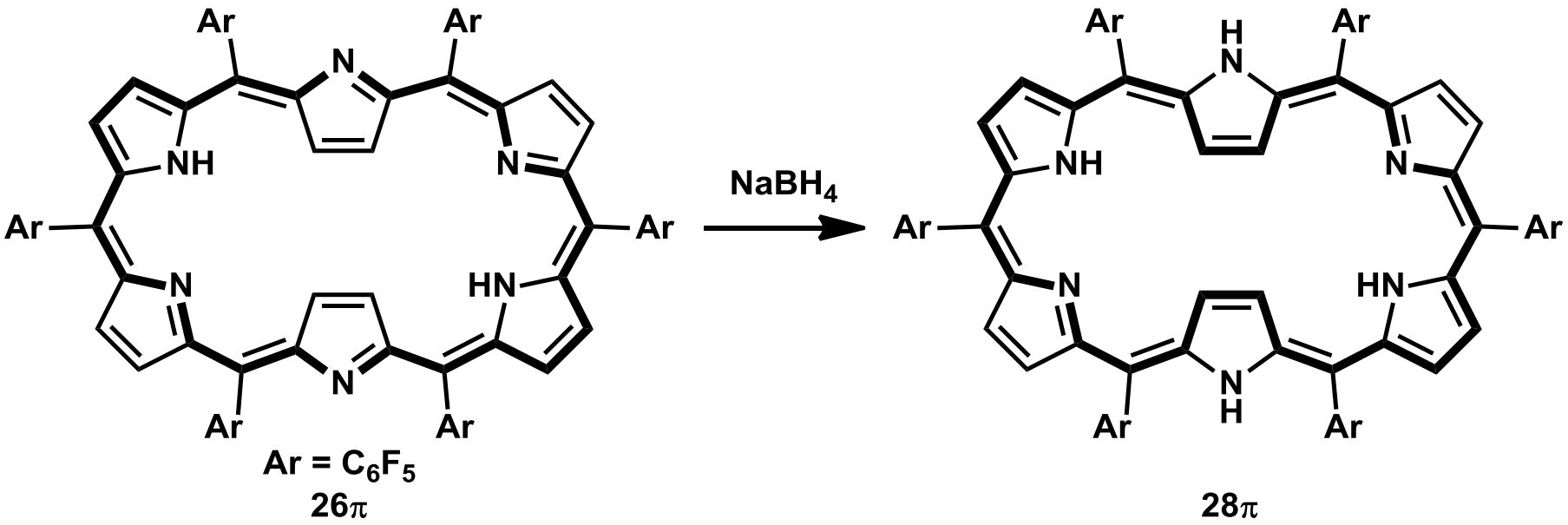


Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 681.

Expanded Porphyrins with a Möbius Aromaticity (7)

Conformational Equilibrium

synthesis



M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* **1999**, 385.

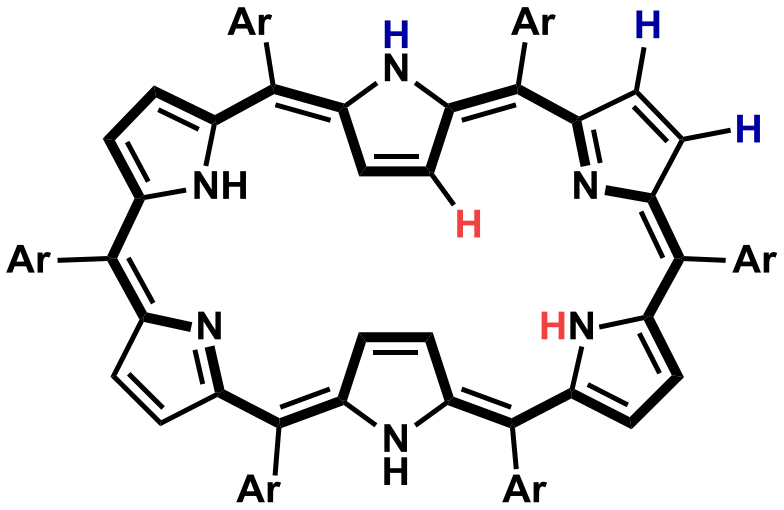
J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

Expanded Porphyrins with a Möbius Aromaticity (8)

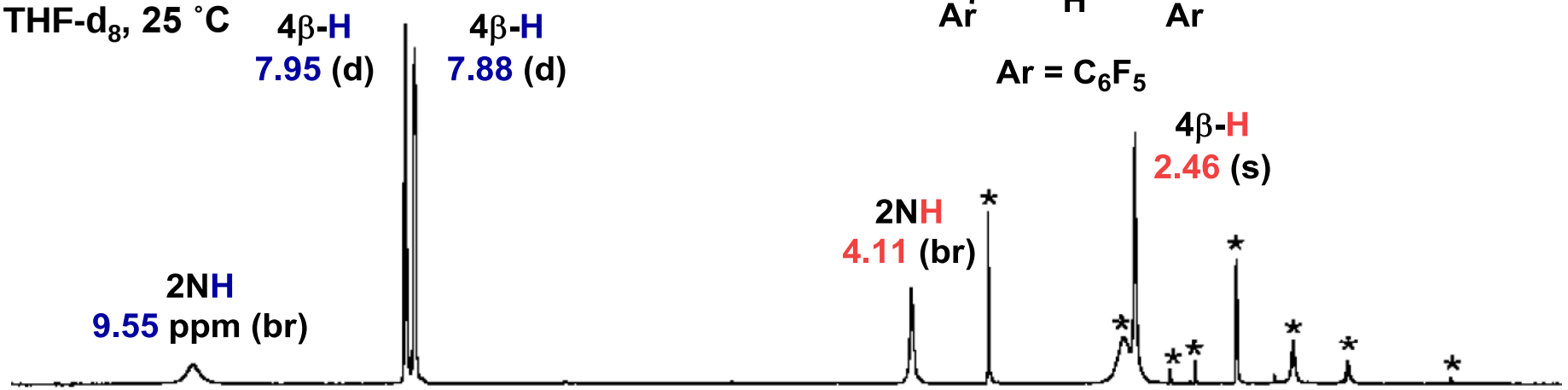
Conformational Equilibrium

^{1}H NMR spectrum

[28]hexaphyrin is planar rectangular conformation and exhibits a moderate diatropic ring current???



Ar = C_6F_5



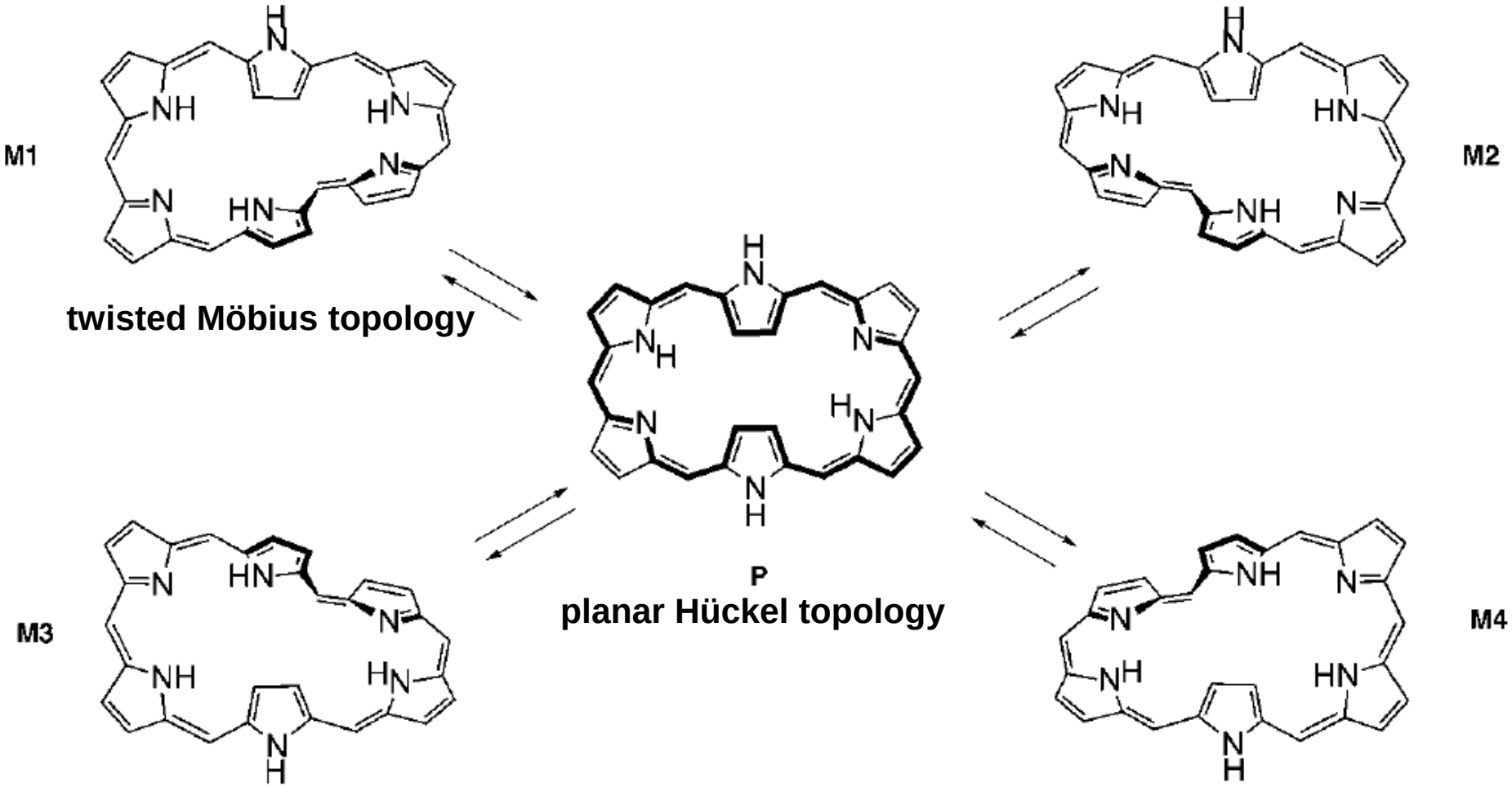
*Peaks marked with * are due to residual solvents and impurities.

J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

Expanded Porphyrins with a Möbius Aromaticity (9)

Conformational Equilibrium

plausible conformational changes

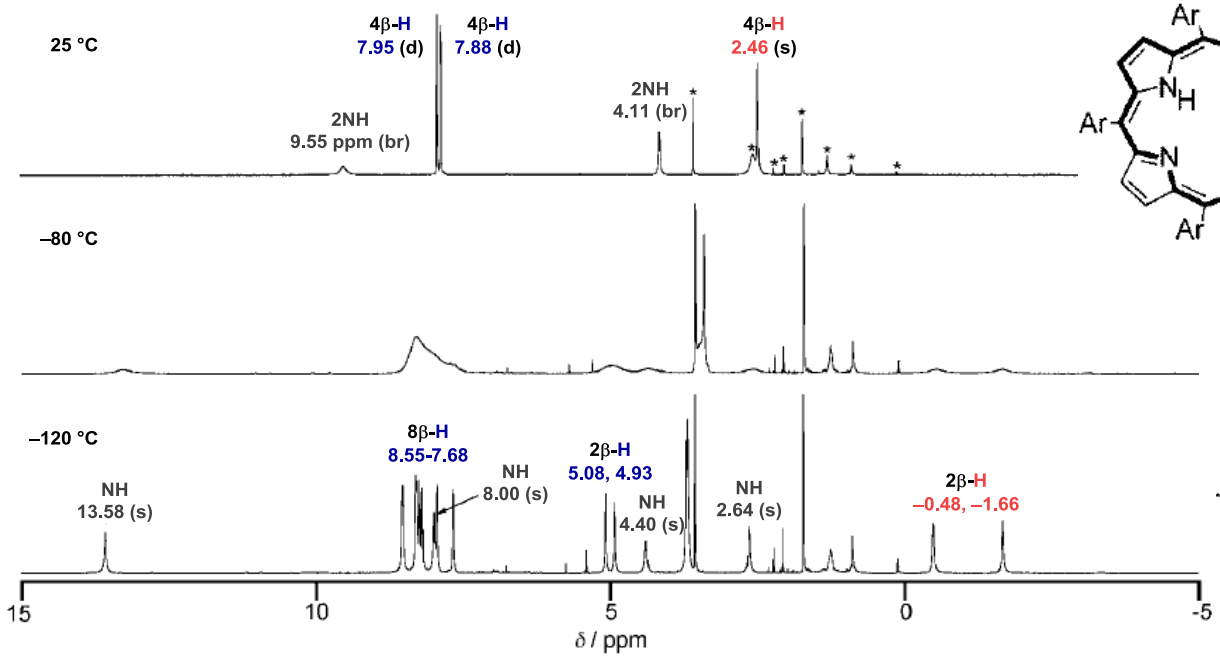


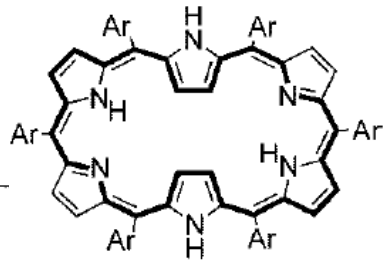
J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

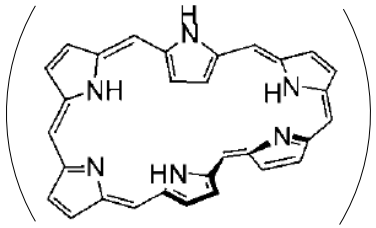
Expanded Porphyrins with a Möbius Aromaticity (10)

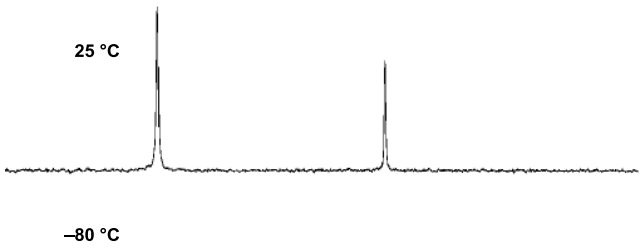
Conformational Equilibrium

NMR spectra

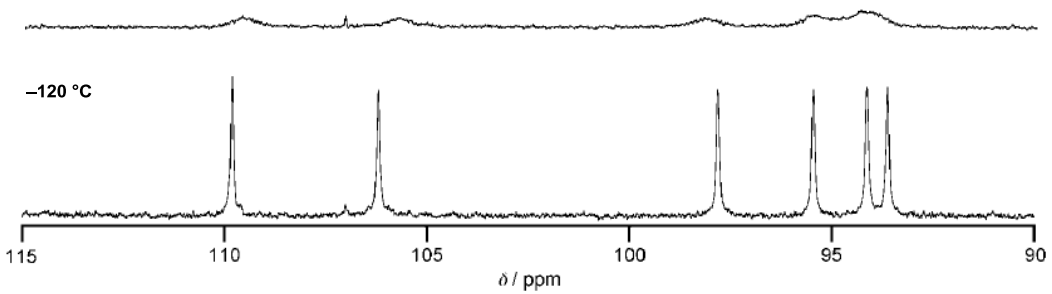








^{1}H NMR spectra of [28]hexaphyrin in THF-d_8. Peaks marked with * are due to residual solvents and impurities.

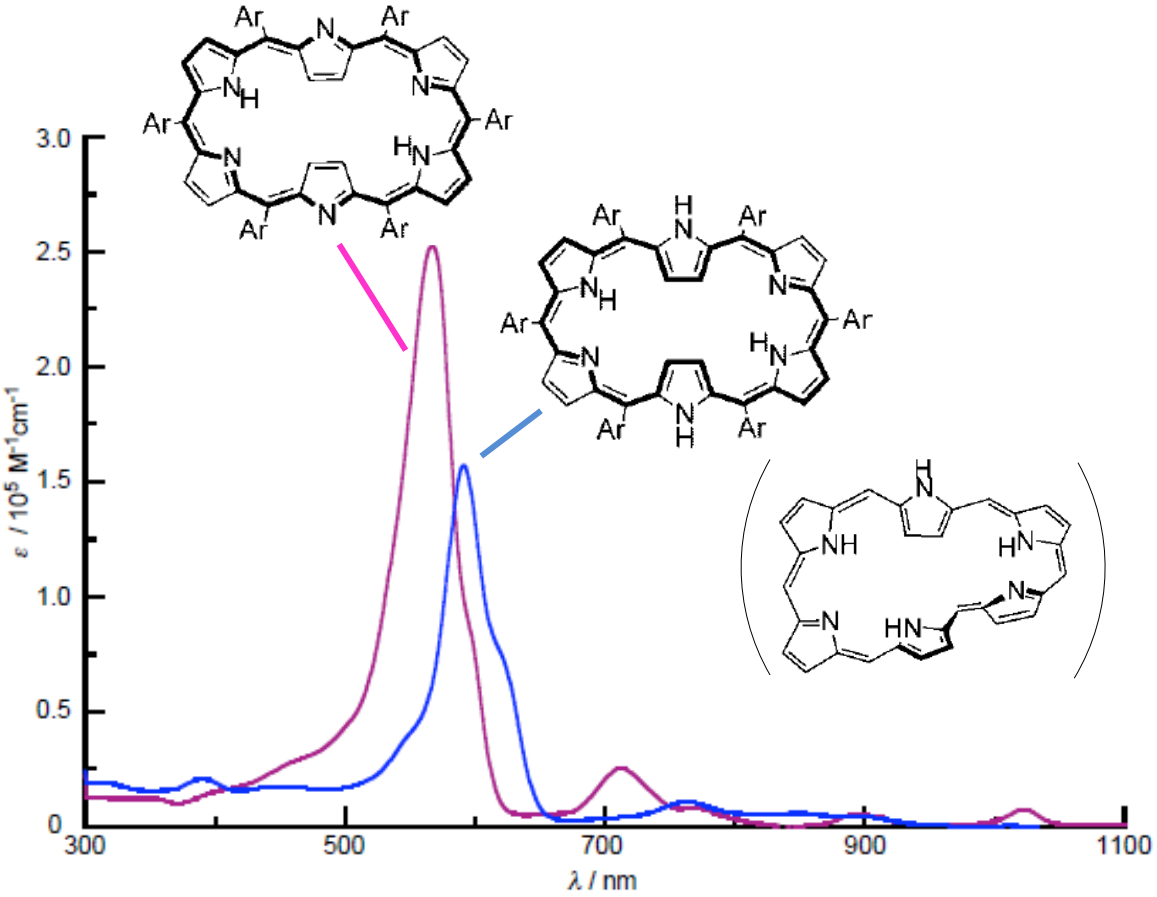


^{13}C NMR spectra of [28]hexaphyrin in THF-d_8.

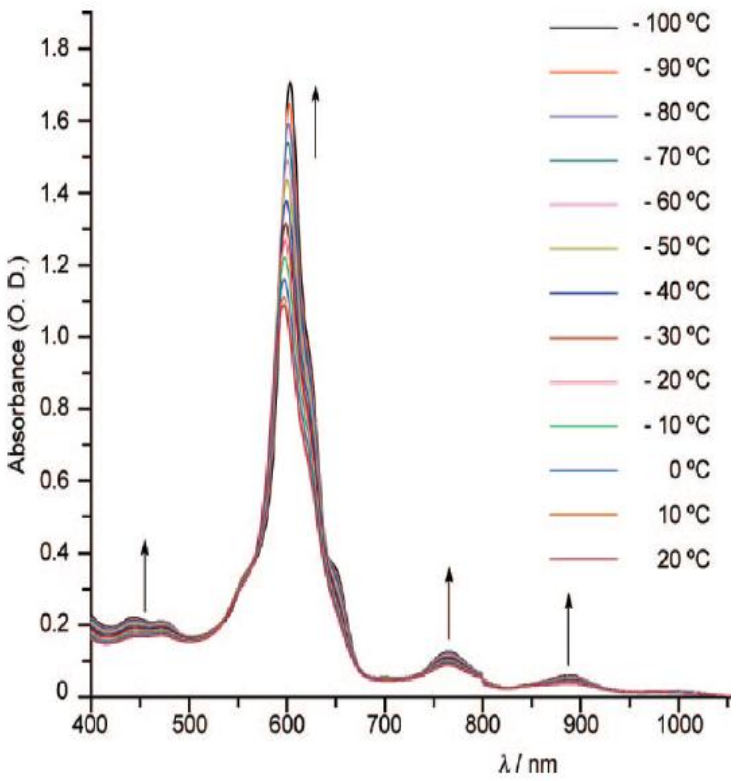
J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

Expanded Porphyrins with a Möbius Aromaticity (11)

Conformational Equilibrium absorption spectra



UV/vis spectra in CH_2Cl_2.



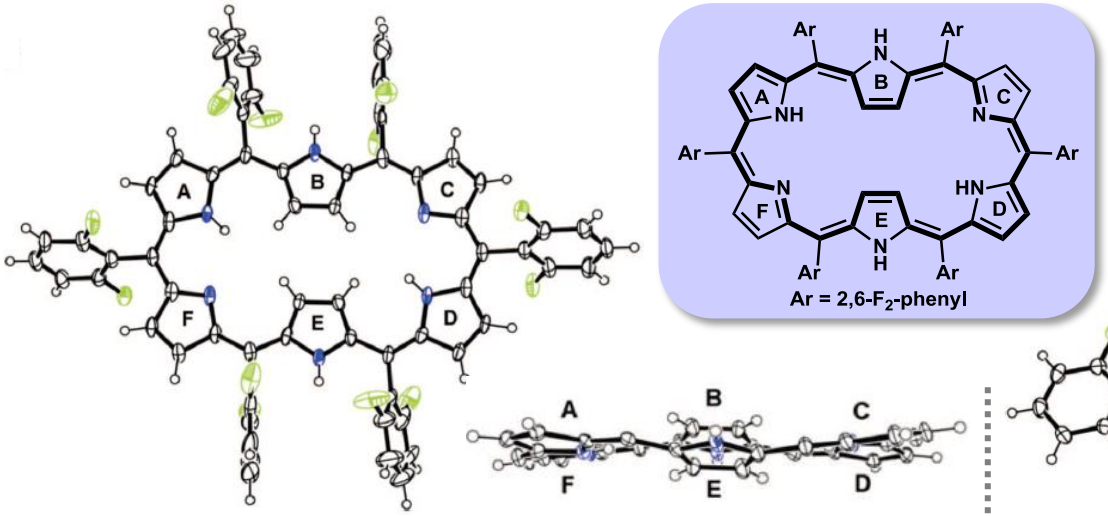
Variable-temperature UV/vis spectra in THF.

J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

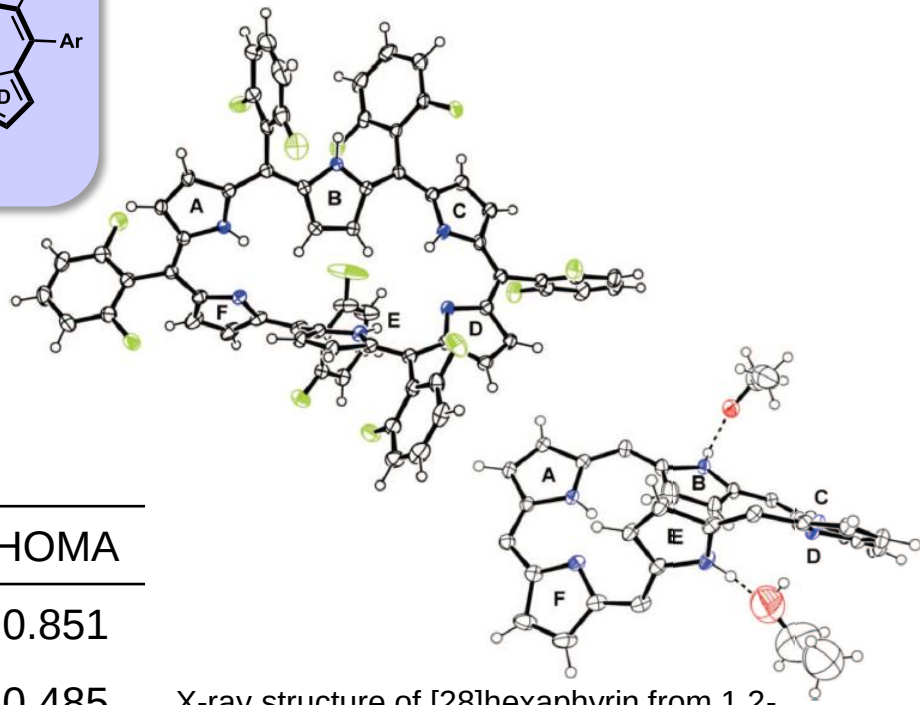
Expanded Porphyrins with a Möbius Aromaticity (12)

Conformational Equilibrium

X-ray structure and theoretical calculations



X-ray structure of [28]hexaphyrin from $CHCl_3$/*n*-heptane: top view and side view.



X-ray structure of [28]hexaphyrin from 1,2-dichloroethane/ethanol: top view and side view including hydrogen-bonded ethanol molecules.

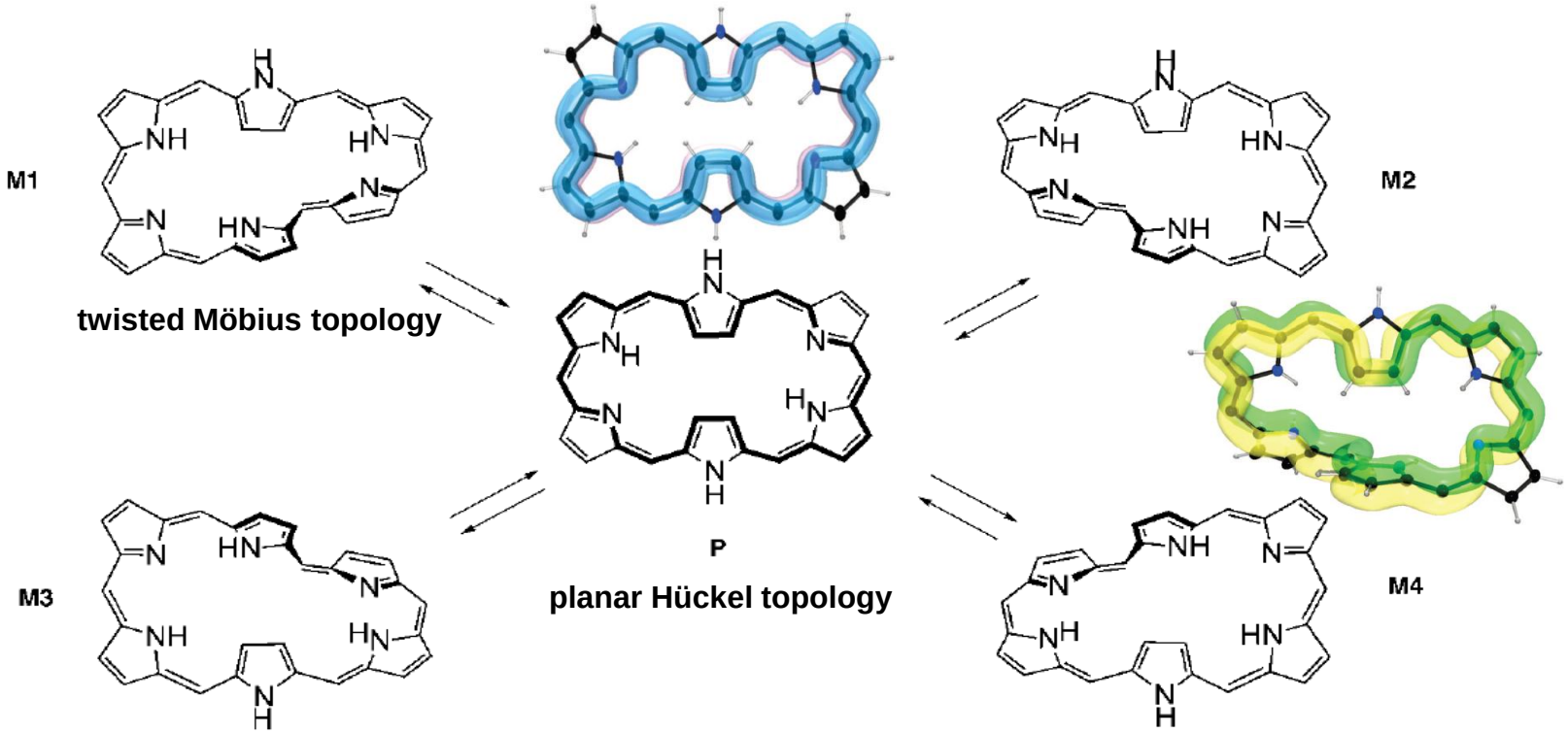
	ΔR_{C-C} (Å)	NICS (ppm)	HOMA
28π Möbius*	0.073	-	0.851
28π Hückel*	0.122	-	0.485
28π Möbius (cal.)**	0.079	–15.2	0.713

*[28]hexaphyrin (Ar = 2,6-F_2-phenyl). **All of the aromatic substituents were replaced by hydrogens.

J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

Expanded Porphyrins with a Möbius Aromaticity (13)

Conformational Equilibrium conclusion



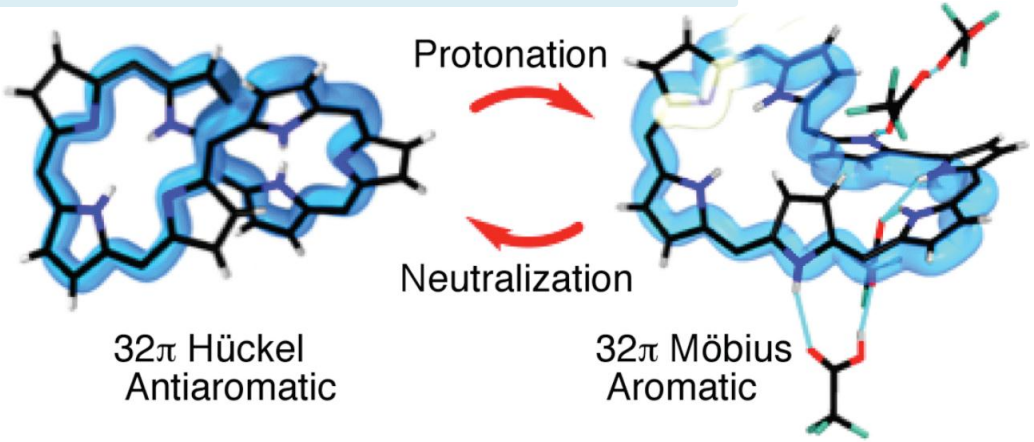
“meso-aryl-substituted [28]hexaphyrins(1.1.1.1.1.1) have been shown to exist in solution at 25 ˚C largely as an equilibrium of several rapidly interconverting twisted Möbius conformations with distinct aromaticities, with a small contribution from a rectangular conformation with antiaromatic character.”

J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568.

Expanded Porphyrins with a Möbius Aromaticity (14)

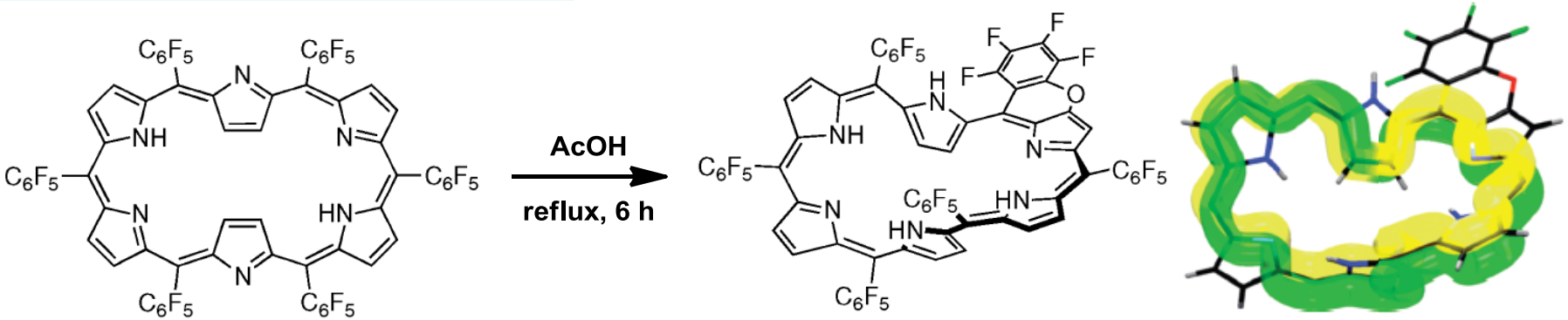
Other Topics

protonation/neutralization switching



S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 9657.

intramolecular fusion reactions



S. Tokuji, J.-Y. Shin, K. S. Kim, J. M. Lim, K. Youfu, S. Saito, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2009**, *131*, 7240.

Summary and Outlook (1)

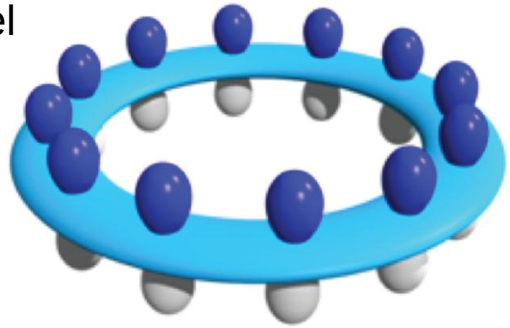
Summary

Criteria of Aromaticity

1. Chemical behavior–electrophilic aromatic substitution.
2. Structural–bond length equalization due to cyclic delocalization.
3. Energetic–enhanced stability (large resonance energy).
4. Magnetic–ring current effects.
   - 1H NMR chemical shifts
   - diamagnetic susceptibility exaltation (Λ)
   - NICS

1964 Heilbronner
Implications of Möbius Aromaticity

Hückel



$(4n+2)\pi$: aromatic

$4n\pi$: antiaromatic

Möbius

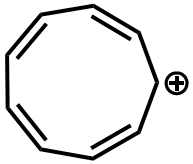
$4n\pi$: aromatic

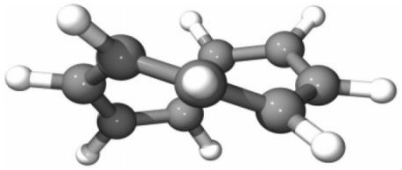
$(4n+2)\pi$: antiaromatic

Summary and Outlook (2)

1998 Schleyer et al.
A Cationic Möbius Aromatic System (calculation)

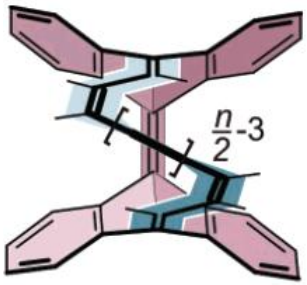
Eight-electron monocyclic cation $(CH)_9^+$ actually does prefer C_2-symmetrical structure and is Möbius aromatic rather than nonaromatic.



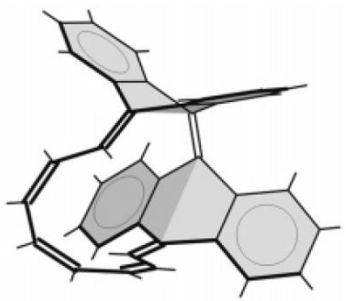


2003 Herges et al.
Synthesis and Properties of a Möbius Cycloalkene

Though Herges says that the C_2 Möbius structure is moderately aromatic, [16]annulene core of C_2 Möbius is nonaromatic.



Möbius

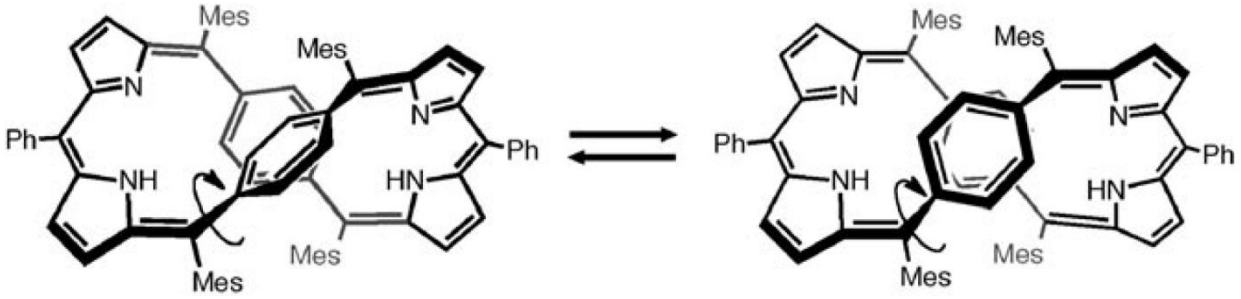


C_2 Möbius

Summary and Outlook (3)

2007 Grażyński et al.
Expanded Porphyrin with a Hückel-Möbius Topology Switch

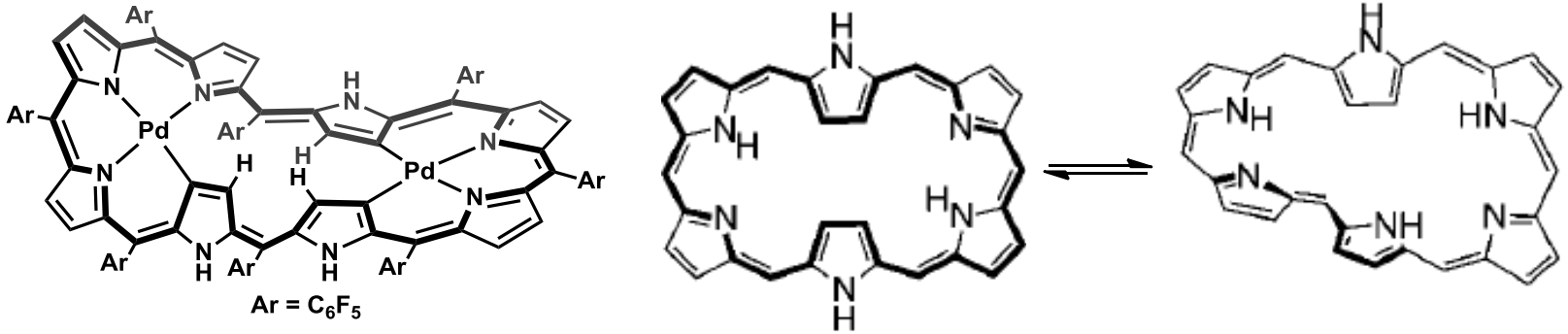
A,D-di-*p*-benzi[28]hexaphyrin(1.1.1.1.1.1) is the first example of dynamic switching between Hückel and Möbius topologies in a conjugated molecule.



Möbius topology Hückel topology

2008 Osuka et al.
Expanded Porphyrins with a Möbius Aromaticity

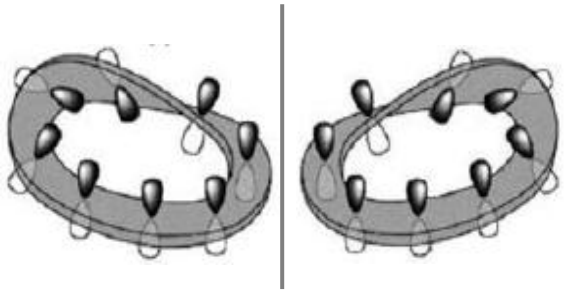
Some expanded porphyrins were the first examples of the molecules which have distinct Möbius aromaticity.



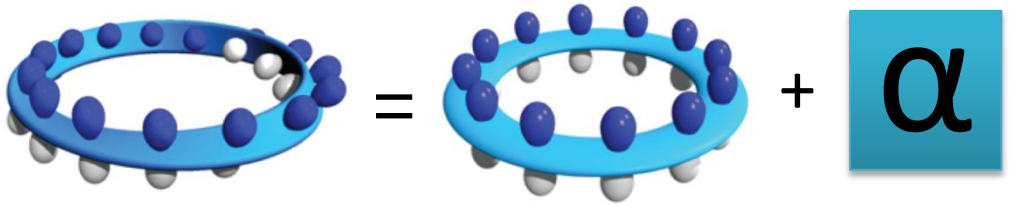
Summary and Outlook (4)

Outlook

Chirality



New Properties



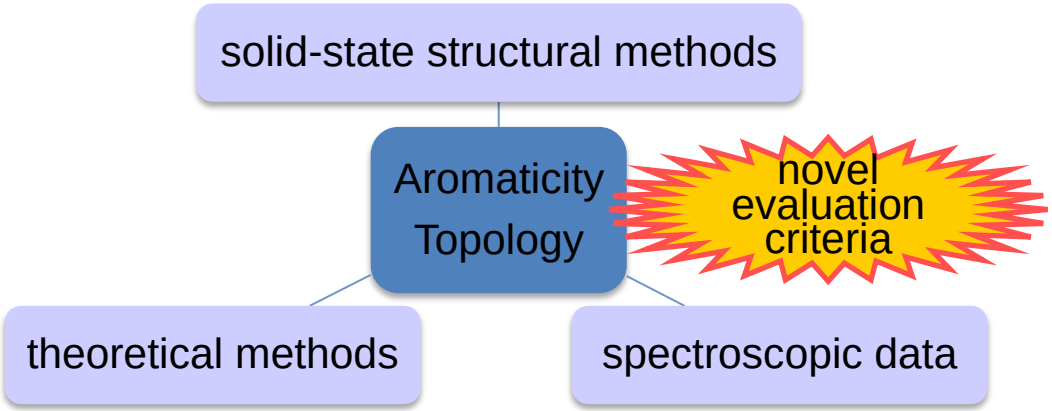
properties of $4n\pi$ aromatic compounds

properties of $(4n+2)\pi$ aromatic compounds

Möbius Antiaromaticity

$(4n+2)\pi$ **anti**aromaticity

Novel Evaluation Criteria for Aromaticity and Topology



References

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R. Herges, *Chem. Rev.* **2006**, *106*, 4820.
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