ORGANIC
LETTERS

2010
Vol. 12, No. 8
1708–1711

The [13]Annulene Cation Is a Stable Möbius Annulene Cation

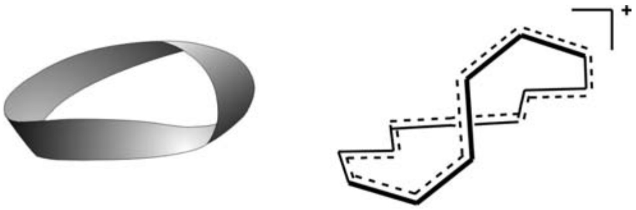
Eva-Katrin Mucke, Felix Köhler, and Rainer Herges*

*Otto-Diels-Institute of Organic Chemistry, Christian-Albrechts-University Kiel,
24098 Kiel, Germany*

rherges@oc.uni-kiel.de

Received January 29, 2010

ABSTRACT



The isomers of the [*n*]annulene cation series (*n* = 13, 17, and 21) were systematically scrutinized by DFT, SCS-MP2, and coupled-cluster methods. Only in the case of the [13]annulene cation the global minimum is clearly a Möbius structure. According to our theoretical predictions, the [13]annulene cation should also be kinetically stable. Thus, the [13]annulene cation is the most promising candidate for the synthesis of a parent Möbius aromatic system among the neutral and cationic annulenes.

After Heilbronner's prediction in 1964 that a 180° twist in [4*n*]annulenes should lead to stable Möbius π systems,[1] several theoretical groups presented hypothetical [4*n*]electron Möbius annulenes that are almost as strongly aromatic as benzene.[2] It is now generally accepted that the Möbius twist reverses the Hückel rules. However, it took until 2003 when the first Möbius annulene was synthesized.[3] Meanwhile Osuka et al. prepared a number of extended Möbius porphyrins that are strongly aromatic with 4*n* electrons delocalized in the cyclic π conjugation path. Möbius aromaticity even seems to be a driving force inducing the twist in larger systems where the twist in the ring can be accommodated without building up too much strain.[4] However, in simple unsubstituted neutral annulenes the energy gained from Möbius aromaticity does not outmatch the strain induced by the twist. The most stable isomer in the series of [12]-, [16]-, and [20]annulenes each is a Hückel (antiaromatic) structure. Unfortunately, there is little chance to synthesize a (higher energy) Möbius isomer, even at very low temperatures. [4*n*]Annulenes are extremely flexible structures that undergo very fast *cis*−*trans* isomerizations and bond shifts.[5] A hypothetical Möbius structure, driven by the relief of ring strain, would rapidly untwist, losing Möbius aromaticity. In our search for a stable Möbius annulene we therefore systematically scrutinized the [13]-, [17]-, and [21]annulene cations.[6] Whereas the smallest [4*n*]annulene cation, the cyclopentadiene cation, is obviously too small to include a twist in the ring, a strongly aromatic

---

(1) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923–1928.

(2) (a) Castro, C.; Isborn, C. M.; Karney, W. L.; Mauksch, M.; Schleyer, P. v. R. *Org. Lett.* **2002**, *4*, 3431–3434. (b) Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697–3715.

(3) (a) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819–821. (b) Ajami, D.; Hess, K.; Köhler, F.; Näther, C.; Oeckler, O.; Simon, A.; Yamamoto, C.; Okamoto, Y.; Herges, R. *Chem.—Eur. J.* **2006**, *12*, 5434–5445. (c) Herges, R. *Chem. Rev.* **2006**, *106*, 4820–4842.

(4) (a) Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z. S.; Kim, K. S.; Noh, S. B.; Park, J. K.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 681–696. (b) Park, J. K.; Yoon, Z. S.; Yoon, M.-C.; Kim, K. S.; Mori, S.; Shin, J.-Y.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2008**, *130*, 1824–1825. (c) Sankar, J.; Mori, S.; Saito, S.; Rath, H.; Suzuki, M.; Inokuma, Y.; Shinokubo, H.; Kim, K. S.; Yoon, Z. S.; Shin, J.-Y.; Lim, J.; Matsuzaki, Y.; Matsushita, O.; Muranaka, A.; Kobayashi, N.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 13568–13579. (d) Saito, S.; Shin, J.-Y.; Lim, J. M.; Kim, K. S.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9657–9660.

(5) (a) Pemperton, R. P.; Gutierrez, M. G.; Castro, C.; Karney, W. L. *J. Am. Chem. Soc.* **2006**, *128*, 16692–16700. (b) Moll, J. F.; Pemberton, Ryan, P.; Gutierrez, M. G.; Castro, C.; Karney, W.; William, L. *J. Am. Chem. Soc.* **2007**, *129*, 274–275.

(6) Mauksch, M. Dissertation, Universität Erlangen-Nürnberg, 1999. He calculated several [13]annulene cations; however, different isomers are presented here.

10.1021/ol1002384

Möbius [9]annulene cation was considered to be an intermediate in the solvolysis of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene.[7] However, more recent calculations revealed that the most stable Hückel and the most stable Möbius monocyclic $(CH)_9^+$ isomer are almost isoenergetic.[8] In LFP experiments only the Hückel isomer was identified. Moreover, the [9]annulene cation intermediate is extremely short-lived since it rapidly undergoes electrocyclic ring closure to form a [4.3]bicyclic cation. So far it escaped direct observation by NMR and even trapping reactions.

We now present evidence based on theoretical calculations that the next higher homologue in the series of [4*n*]annulene cations, the [13]annulene cation, probably is the only unsubstituted annulene that is thermodynamically and kinetically stable enough to be synthesized or at least to be identified by trapping reactions.

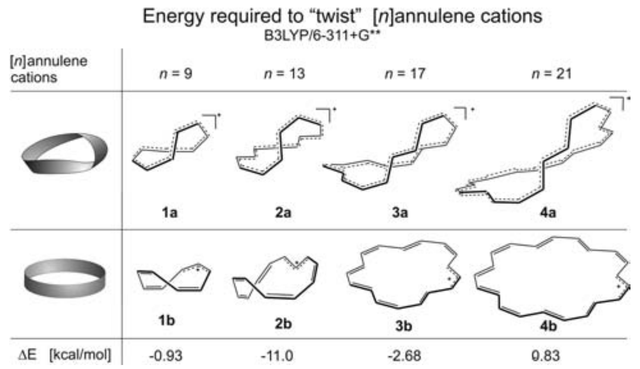


Figure 1. Relative energies of the most stable Hückel and Möbius isomer of [9]-, [13]-, [17]-, and [21]annulene cations at the B3LYP/6-311+G** level of theory. The structures are two-dimensional representations of the optimized geometries (B3LYP/6-311+G**) of the most stable isomer of both topologies in each series of annulenes. The hydrogen atoms are omitted for clarity. The positive charge is almost equally delocalized in the aromatic Möbius annulenes but more or less localized in an allyl- or pentadienyl unit in the antiaromatic Hückel systems.

A Monte Carlo algorithm was used to generate a large number of isomers of each [4*n*]annulene cation.[9] After eliminating redundancy, PM3[10] calculations were performed. Energy cut-offs were set to reduce computational cost. The most stable isomers[11] were optimized using the DFT methods KMLYP,[12] BH&HLYP,[13] and B3LYP[14] and a 6-311+G** basis set.[15] The [13]annulene cation structures were also calculated using the cc-pVTZ[16] basis set.[17] It is known that DFT methods suffer from the self-interaction error that leads to the overestimation of the stability of delocalized systems.[18] Therefore, we optimized the most stable Hückel and Möbius structure of the [13]annulene and [17]annulene cation at the B2PLYP/6-311+G**[19] and SCS-MP2/def2-TZVP[20,21] level of theory. The [21]annulene cations were optimized at B2PLYP/6-31G*. According to previous calculations on the [9]annulene cation[7] B3LYP/6-311+G** was closest in

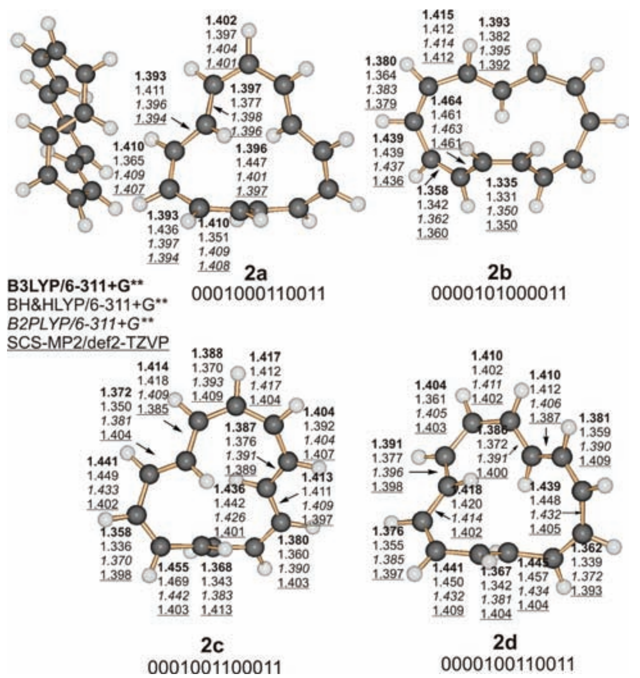


Figure 2. Geometries of the most stable Möbius structure **2a** (C_2), the most stable Hückel isomer **2b** (C_s), and the second and third most stable isomers of the [13]annulene cation **2c** (C_1) and **2d** (C_1). C−C bond lengths are given in angstroms for different levels of theory. The binary numbers indicate the *cis* (0), *trans* (1) configuration of each bond in each structure.

---

(7) (a) Barborak, J. K.; Su, T.-M.; Schleyer, P. v. R.; Boche, G.; Schneider, G. *J. Am. Chem. Soc.* **1971**, *93*, 279–281. (b) Anastassiou, A. G.; Yakali, E. *J. Am. Chem. Soc.* **1971**, *93*, 3803–3805. (c) Anastassiou, A. G.; Yakali, E. *J. Chem. Soc. Chem,. Commun* **1972**, *9*, 531–532. (d) Yakali, E. Dissertation, Syracuse University, 1973. (e) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem.* **1998**, *110*, 2515−1517; *Angew. Chem., Int. Ed.* **1998**, *37*, 2395−2397.

(8) (a) Bucher, G.; Grimme, S.; Huehnerbein, R.; Auer, A. A.; Mucke, E.; Köhler, F.; Siegwarth, J.; Herges, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9971–9974.

(9) Köhler, F. Dissertation, Institut für Organische Chemie, Universität Kiel, 2008.

(10) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221–264. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209–220.

(11) $(CH)_{13}^+$: 2423 isomers; energy cutoff, 140 kcal/mol. $(CH)_{17}^+$: 1839 isomers; energy cutoff, 36 kcal/mol. $(CH)_{21}^+$: 500 isomers; energy cutoff, 19 kcal/mol. Isomers that were higher in energy as the energy cutoff relative to the global minimum were discarded.

(12) (a) Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *115*, 11040–11051. (b) Senosiain, J. P.; Han, J. H.; Musgrave, C. B.; Golden, D. M. *Faraday Discuss* **2001**, *119*, 173–189. (c) The KMLYP functional was specified by including the following keywords in the Gaussian 03 input files: BLYP iop(3/76=1000005570), iop(3/77=0000004430), iop(3/78=0448010000).

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206.

(14) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5642. (b) Lee, C.; Yang, W.; Parr, E. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(15) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. (b) Hehre, W. J.; Dichtfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.

(16) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371. (c) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(17) Calculation were carried out using Gaussian 03, Revision B.04. Frisch M. J. et al., Gaussian Inc., Wallingford, CT, 2004; for full citation see the Supporting Information.

Table 1. Relative Energy of the Most Stable Möbius (**2a**) and Hückel (**2b**) Conformation of the [13]Annulene Cation. The Relative Energies of the Second (**2c**) and Third (**2d**) Most Stable Isomer (Both Möbius) Are Also Included

	topology[a]	**2a** M C_2	**2b** H C_s	**2c** M C_1	**2d** M C_1
level	basis set	E_{rel}	E_{rel}	E_{rel}	E_{rel}
B3LYP[b]	6-311+G**	0.00	11.0	5.20	7.61
BH&HLYP[b]	6-311+G**	0.00	7.68	2.68	5.40
KMYLP[b]	6-311+G**	0.00	8.03	3.49	5.89
B3PW91	6-311+G**	0.00	11.9	5.71	7.87
B2PLYP[c]	6-311+G**	0.00	12.8	6.69	9.06
B3LYP[b]	cc-pVTZ	0.00	11.1	5.13	7.54
BH&HLYP[b]	cc-pVTZ	0.00	7.74	2.61	5.30
KMLYP[b]	cc-pVTZ	0.00	8.73	3.62	5.99
SCS-MP2[c]	def2-TZVP	0.00	14.0	8.63	11.4
CCSD(T)[c]SCS-MP2	cc-pVTZ//def2-TZVP	0.00	9.97		
HOMA[d]		0.73	0.49	0.55	0.59
NICS[e]		−8.95	−9.19	−5.35	−5.35
χ[f]		−111.4	−83.3	−91.9	−97.7
Λ[g]		−28.1	0.00	−8.6	−14.4

[a] Topology of the isomers: M = Möbius, H = Hückel. [b] E_{rel} (kcal/mol): relative energy with respect to the energetically most stable structure after ZPE corrections at the same level of theory. [c] E_{rel}: relative energy with respect to the energetically most stable structure includig ZPE corrections at the B3LYP/6-311+G** level of theory. [d] HOMA index (BH&HLYP/6-311+G**//BH&HLYP/6-311+G**). [e] NICS was computed at GIAO/BH&HLYP/6-311+G**//BH&HLYP/6-311+G**.[22] [f] Magnetic susceptibility (cgs-ppm) calculated with CSGT as implemented in G03 at BH&HLPY/6-311+G**//BH&HLPY/6-311+G**. [g] Magnetic susceptibility exaltation (cgs-ppm) relative to **2b**.

energy to the "gold standard" CCSD(T)/CBS among several other DFT methods. Unfortunately, the [13]-, [17]-, and [21]annulenes are too large systems to be optimized by coupled cluster methods. Therefore, the corresponding B3LYP/6-311+G** energies are given in Figure 1.

[13]Annulene Cation. The global minimum **2a** is an aromatic penta-*trans* structure with Möbius topology (NICS = −8.95) (see Figures 1 and 2, and Table 1).

Interestingly, besides the C_2-symmetric Möbius isomer there are two different penta-*trans* Möbius species **2c** and **2d** that are 5.20 and 7.61 kcal/mol higher in energy (B3LYP/6-311+G**). Their negative NICS values (−5.35 and −5.35) indicate Möbius aromatic properties. The most stable Hückel annulene,[23] the C_s symmetric tetra-*trans* isomer **2b**, is 11.0 kcal/mol higher in energy as the (global) Möbius minimum **2a**. This Hückel isomer **2b** revealed nonaromatic properties such as a HOMA value of 0.49. The magnetic susceptibility of the Möbius structure **2a** is −28.1 (cgs-ppm) relative to Hückel isomer **2b** indicating strong aromaticity (HOMA of **2a**: 0.73).

Furthermore, CCSD(T) single-point calculations[24] for the SCS-MP2 optimized isomers (**2a** and **2b**) were carried out. With an energy difference of 10.0 kcal/mol in favor of the Möbius isomer **2a** the thermodynamical stability of the Möbius relative to the most stable Hückel species (**2b**) determined at the DFT levels is corroborated (Table 1).

The distinct relative stability of the Möbius structure not withstanding, the reactivity of this species might be very high and its synthesis and characterization thus could turn out to be difficult or even impossible. The [9]annulene cation escapes characterization and trapping by a very rapid electrocyclic ring closure forming a thermodynamically more stable bicyclic structure. Most favorable in case of the [13]annulene cation is the formation of [8.3.0]bicyclic system which could undergo further ring closing to a [7.4.0.0^{2,6}] tricyclic ring (Scheme 1). We calculated a number of electrocyclic ring closure reactions (starting from different isomers of the [13]annulene cation). The thermodynamically most favorable reaction is shown in Scheme 1 (for more details, see the Supporting Information). With a barrier of more than 23 kcal/mol toward ring closure for all calculated modes of electrocyclic reactions, **2a** should be kinetically

---

(18) (a) Schreiner, P. R. *Angew. Chem.* **2007**, *119*, 4295−4297; *Angew. Chem. Int. Ed* **2007**, *46*, 4217−4219. (b) Lundberg, M.; Sigbahn, P. E. M. *J. Chem. Phys.* **2005**, *122*, 224103. (c) Mori-Sanchez, P.; Cohen, A. J.; Yang, W. *J. Chem. Phys.* **2006**, *125*, 201102. (d) Ball, T.; Sastry, G. N. *J. Phys. Chem. A* **1997**, *101*, 7923–7925.

(19) (a) Grimme, S. J. *J. Chem. Phys.* **2006**, *124*, 34108. (b) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397.

(20) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095–9102.

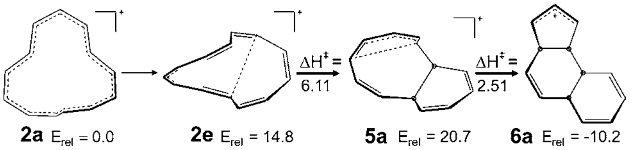
(21) (a) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem, Phys.* **2005**, *7*, 3297–3305.

(22) (a) The nucleus independent chemical shifts of **2a** and **2b** are probably dominated by strong local effects. (b) The ghost atom for the NICS calculation is very close to neighboring hydrogen atoms (0.968 Å), this is also the case for NICS(1) (1.328 Å). (c) Martin, N. H.; Brown, D. *Int. J. Mol. Sci.* **2000**, *1*, 84, and references cited. (d) Wannere, C. S.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 865–868. (e) Pelloni, S.; Ligabue, A.; Lazzeretti, P. *Org. Lett.* **2004**, *6*, 4451–4454. (f) Soriana, J. R.; Ligabue, A.; Soncini, A.; Lazzeretti, P. *J. Phys. Chem. A* **2002**, *106*, 11806.

(23) At the BH&HLYP/6-311+G** level (and only at this level) an additional Hückel isomer **2i** was located which is 4.54 kcal/mol higher in energy than the global Möbius minimum (see the Supporting Information).

(24) (a) Bartlett, R. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head Gordon, M. *Chem. Lett* **1989**, *157*, 479–483. (c) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 27–35.

Scheme 1. Kinetically Most Favorable Electrocyclization of the [13]Annulene Cation[a]



[a] E_{rel}: relative energy in kcal/mol compared to the most stable structure **2a** after ZPE corrections. $\Delta H^{\ddagger}$: activation barrier in kcal/mol relative to **2a** at B3PW91/6-311+G**.

stable enough for isolation and characterization, at least at low temperatures (compare to 8.1 kcal/mol in case of the [9]annulene at B3LYP/6-311+G**).[7e]

A direct electrocyclization pathway was found for **2a**, which, however, is energetically unfavorable. Several isomers higher in energy (such as **2c**,**f**−**h**, see Supporting Information) also undergo ring closure. The bicyclic products each are more than 14.8 kcal/mol higher in energy than **2a**. Final products that are thermodynamically more stable than **2a** are formed via a second electrocyclization giving rise to tricyclic structures. The most stable tricyclic structure is 10.2 kcal/mol more stable than **2a**.

[17]Annulene Cation. Calculations on the PES of the [17]annulene cation revealed **3a** as the most stable Möbius and **3b** as the most stable Hückel isomer (Figure 3). NICS (−9.40) and HOMA (0.757) values of **3a** (C_1) (BH&HLYP/6-311+G**) clearly indicate strong Möbius aromaticity. In sharp contrast, the C_s-symmetrical, almost planar Hückel configuration **3b** exhibits a HOMA value of 0.585 and a NICS value of 17.6 and thus is clearly antiaromatic.

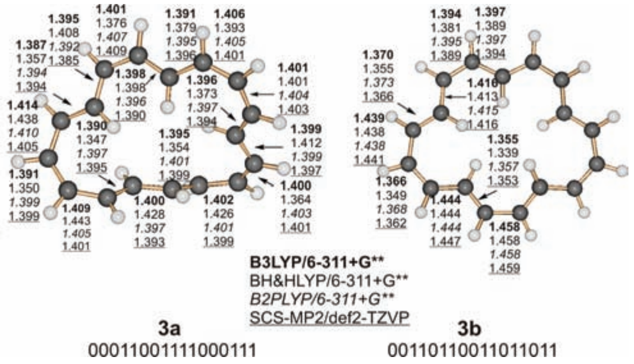


Figure 3. Geometries of the most stable Möbius structure **3a** (C_1, left) and the most stable Hückel species **3b** (C_s, right) of the [17]annulene cation. C−C bond lengths are given in angstroms for different levels of theory. The binary numbers indicate *cis* (0) or *trans* (1) configuration of each bond in each structure.

However, our calculations performed at different levels of theory disagree whether the Hückel or the Möbius isomer is the global minimum of (CH)$_{17}^{+}$. BH&HLYP favors the Hückel structure by 1.85 kcal/mol. B3LYP/6-311+G**, B3PW91/6-311+G**, B2PLYP/6-311+G**, SCS-MP2/def2-TZVP predict the Möbius structure to be more stable by: 2.63, 3.73, 6.01, and 9.60 kcal/mol. Hence, the question remains open whether the [17]annulene is a Hückel or Möbius structure. Unfortunately, coupled cluster methods are (still) too expensive to be applied to the larger annulenes.

[21]Annulene Cation. A thorough investigation of the (CH)$_{21}^{+}$ potential hypersurface revealed **4a** (C_2, HOMA = 0.727, NICS = −6.20) as the most stable Möbius and **4b** (C_s, HOMA = 0.668, NICS = 22.2) as the most stable Hückel isomer (BH&HLYP/6-31G*) (Figure 4). As in the case of the [17]annulene cation our calculations do not exhibit a clear picture whether the Hückel or the Möbius structure is the global minimum among the isomers of the [21]annulene cation. B3LYP/6-311+G** and BH&HLYP/6-311+G** are in favor of the Hückel structure (0.98 and 4.56 kcal/mol), and B3PW91/6-311+G**, B2PLYP/6-31G* predicts the Möbius isomer to be 0.18 kcal/mol, 3.49 kcal/mol more stable.

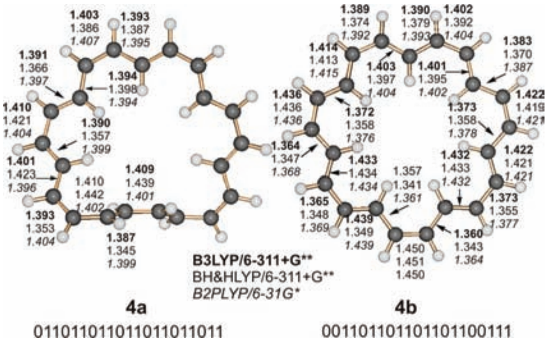


Figure 4. Geometries of the most stable Möbius structure **4a** (C_2, left) and the most stable Hückel species **4b** (C_s, right) of the [21]annulene cation. C−C bond lengths are given in angstroms for different levels of theory. The binary numbers indicate *cis* (0) or *trans* (1) configuration of each bond in each structure.

In conclusion, our calculations predict that among the [9]-, [13]-, [17]-, and [21]annulenes the [13]annulene is by far the most promising candidate for the synthesis of a stable unsubstituted Möbius annulene. Even though several Möbius-extended porphyrins have been recently synthesized[4] such a prototype Möbius annulene is still elusive. According to our calculations on potential electrocyclic reactions (which are experimentally observed for the [9]annulene cation), the [13]annulene cation should also be kinetically stable enough for isolation or at least trapping.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft. We thank one of the reviewers for support.

Supporting Information Available: Details of computational methods, absolute energies, and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OL1002384