ORGANIC LETTERS

2002
Vol. 4, No. 20
3431−3434

Aromaticity with a Twist: Möbius [4*n*]Annulenes

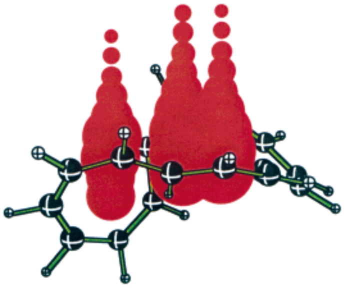
Claire Castro,*,† Christine M. Isborn,† William L. Karney,*,† Michael Mauksch,‡ and Paul von Ragué Schleyer*,‡,§

*Department of Chemistry, University of San Francisco, 2130 Fulton St.,
San Francisco, California 94117, Computer Chemistry Center and
Institute of Organic Chemistry, University of Erlangen-Nuremberg,
Henkestrasse 42, D-91054 Erlangen, Germany, and Department of Chemistry,
University of Georgia, Athens, Georgia 30602*

karney@usfca.edu

Received July 25, 2002

ABSTRACT



Aromatic Möbius [4*n*]annulenes with 4*n* π electrons, originally conceived by Heilbronner, are characterized computationally. These $(CH)_{12}$, $(CH)_{16}$, and $(CH)_{20}$ minima have nearly equal C–C bond lengths, small twist angles around the rings, and magnetic properties (NICS, nucleus-independent chemical shifts—see above at various positions in [16]annulene—and magnetic susceptibility exaltations) indicating significantly diatropic ring currents. The Möbius forms are not the most stable isomers but may contribute significantly to the chemistry of these annulenes.

Heilbronner conceived "Möbius aromaticity" in 1964.[1a] He suggested that large cyclic [4*n*]annulenes might be stabilized if the π orbitals were twisted gradually around a Möbius strip (Figure 1).[1a] Soon afterward, Zimmerman generalized this idea and applied the "Hückel−Möbius concept" to the analysis of ground-state systems such as barrelene, as well as to allowed pathways of electrocyclic reactions.[1b,c] Indeed, geometric, energetic, and magnetic criteria show that both (4*n* + 2)-electron Hückel and 4*n*-electron Möbius transition states of a variety of concerted reactions are aromatic.[2] However, no neutral, fully conjugated annulene with Möbius topology exhibiting aromatic character in the original Heilbronner sense has been reported. Interest was rejuvenated in 1998 by a computational reinterpretation of existing experimental evidence for $(CH)_9^+$, as a Möbius aromatic cyclic annulene with 4*n* π electrons.[3] Bond length equalization, large negative nucleus-independent chemical shifts (NICS),[4] and a substantial magnetic susceptibility exaltation[5] point to the existence of diatropic ring currents in this ion.

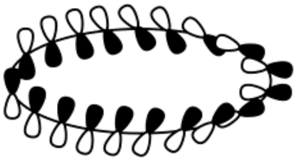


Figure 1. Hypothetical π system with Möbius topology.

[†] University of San Francisco. Email for C.C.: castroc@usfca.edu.
[‡] Institute of Organic Chemistry, University of Erlangen-Nuremberg.
[§] University of Georgia. schleyer@chem.uga.edu.

(1) (a) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923. (b) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564. (c) Zimmerman, H. E. *Accts. Chem. Res.* **1972**, *4*, 272.

(2) See Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 407, and references therein.

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

10.1021/ol026610g CCC: $22.00 © 2002 American Chemical Society
Published on Web 09/11/2002

Very recently, Rzepa and his group have explored applications of the Möbius concept to smaller homocyclic and heterocyclic rings extensively and imaginatively.[6]

Our goal was to locate computationally the first examples of [4*n*]annulenes with significant aromatic character.[7] Not surprisingly, the recent ab initio results of Havenith and coworkers on *trans*-cyclooctatetraene suggested that this formally Möbius species is nonaromatic as a result of, at least in part, poor π overlap.[8] While Rzepa's [16]annulene isomer has a formal Möbius topology, the strong bond-length alternation and the NICS of −0.5 indicate a nonaromatic species.[6a]

Stable Möbius [4*n*]annulenes are attractive targets for computational surveys. Information on such species would augment our knowledge of aromaticity[9] and identify possible synthetic targets. We now present computational results on [12]-, [16]-, and [20]annulene isomers possessing a Möbius half-twist. Our optimized B3LYP/6-31G*[10,11] structures[12,13] of the [12]-, [16]-, and [20]-annulenes are shown in Figures 2−4, respectively. Table 1 summarizes the computed relative energies as well as geometric and magnetic parameters. In addition to the Möbius isomers, data are included for several non-Möbius conformations, a few of which have been proposed previously (vide infra).

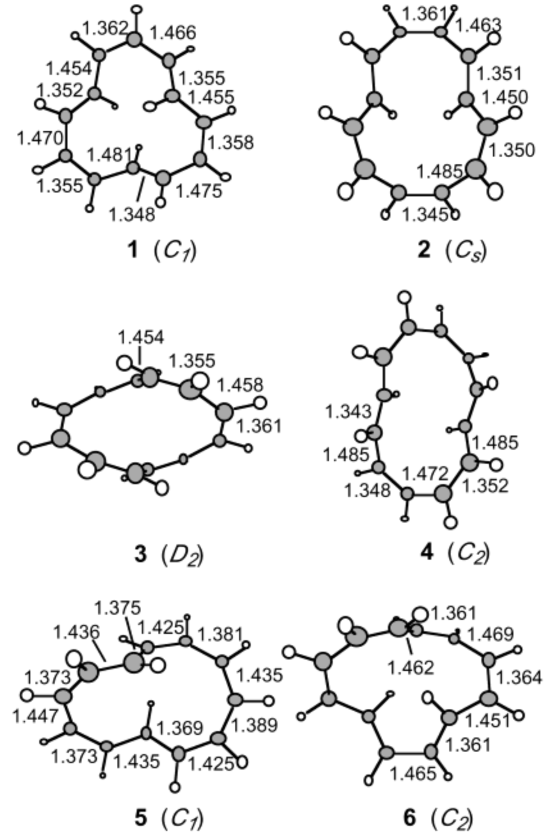


Figure 2. B3LYP/6-31G* optimized geometries of [12]annulene isomers. CC bond lengths are in angstroms.

Geometric criteria for aromaticity in annulenes are quantified by (1) the degree of bond length equalization, i.e., ΔCC, the difference between the longest and shortest C−C bonds in the ring; (2) the Julg parameter, *A*;[14] and (3) the HOMA (harmonic oscillator measure of aromaticity) index.[15] *A* and HOMA values less than 1.0 indicate reduced aromaticity. Both magnetic criteria employed, NICS[4] and magnetic susceptibility exaltations (MSE),[5] are now widely used to evaluate aromaticity. Hückel-type aromatic carbocyclic and heterocyclic systems typically exhibit large negative NICS values (e.g., ca −10 for benzene) and large magnetic susceptibility exaltations.[4] Mizoguchi's formal treatment showed that Möbius annulenes with [4*n*] π electrons also should have enhanced magnetic susceptibilities,[16] but actual molecules were not examined.

[12]Annulenes. The reported [12]annulene, synthesized photolytically at −100 °C by Oth and co-workers,[17] was assigned the putative structure **1** (Figure 2) on the basis of NMR data. The products of photochemical and thermal reactions were explained by assuming that **1** was in dynamic equilibrium with **2**.[17] The optimized geometries of **1** and **2**

---

(4) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. See also: (b) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.

(5) (a) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, pp 167−206. (b) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811. (c) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991.

(6) (a) Martín-Santamaria, S.; Lavan, B.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1415. Also see: (b) Martín-Santamaria, S.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2372. Martín-Santamaria, S.; Lavan, B.; Rzepa, H. S. *Chem. Commun.* **2000**, 1089. (c) Karney, W. L.; Kastrup, C. J.; Oldfield, S. P.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2002**, 388. (d) Kastrup, C. J.; Oldfield, S.; Rzepa, H. S. *Chem. Commun.* **2002**, 642.

(7) (a) However, see: Mauksch, M.; Dissertation, University of Erlangen-Nuremberg, 1999. Supporting computations were carried out at Erlangen by Valentin Gogonea and Ralph Puchta. (b) [*n*]Trannulenes, with a full twist and all p-π orbitals in-plane, are [4*n* + 2] aromatics: Fokin, A. A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 9364. (c) Neutral, planar annulene triplets with [4*n*] π electrons also are aromatic: Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945.

(8) Havenith, R. W. A.; van Lenthe, J. H.; Jenneskens, L. W. *Int. J. Quantum Chem.* **2001**, *85*, 52.

(9) For recent reviews, see: Schleyer, P. v. R. special editor, *Chem. Rev.* **2001**, *101*, 1115−1566.

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

(11) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(13) All reported species are minima, with no imaginary vibrational frequencies. Topologies were assigned by tracing the π system along one face of the ring: return to the starting point on the same face of the ring indicates Hückel topology, while return to the opposite face of the ring indicates Möbius topology. Species with a CCCC dihedral angle deviating by more than 75° from 0° or 180° are considered to have neither Hückel nor Möbius topology, as significant cyclic π delocalization is precluded.

(14) Julg, A.; Francois, P. *Theor. Chim. Acta* **1967**, *7*, 249.

(15) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, 3839. Also, Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70. Krygowski, T. M.; Cyranski, M. *Tetrahedron* **1996**, 1713.

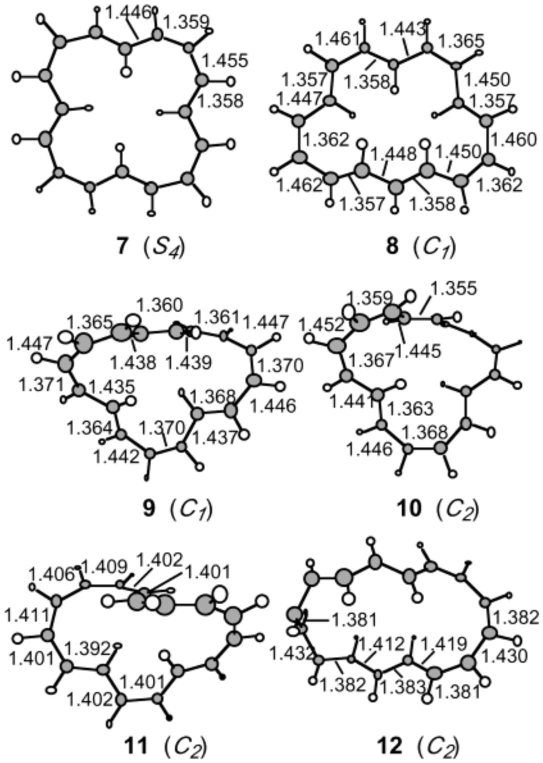
(16) Mizoguchi, N. *Chem. Phys. Lett.* **1987**, *134*, 371.

(17) Oth, J. F. M.; Röttele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, 61.

Table 1. Relative Energies (kcal/mol) and Selected Geometric (B3LYP/6-31G*) and Magnetic Data for [4*n*]Annulenes

cmpd	sym	topol[a]	rel *E*[b]	ΔCC[c]	Julg, *A*[d]	HOMA[e]	NICS(0) [(1)][f]	χ[g]	Λ[h]	∠CCCC[i]
					[12]Annulenes					
1	C_1	H	0.0	0.133	0.64	0.04	+3.2 [+2.0]	−65.0	0.0	62.4
2	C_s		3.8	0.140	0.63	0.01	−2.4 [−1.7]	−77.9	−12.9	79.5
3	D_2	H	−0.3	0.103	0.72	0.27	−8.1 [−9.7]	−83.3	−18.3	40.9
4	C_2		2.5	0.142	0.50	−0.32	−4.9 [−1.9]	−58.7	+6.3	79.0
5	C_1	M	4.4	0.078	0.90	0.69	−14.6 [−12.7]	−101.5	−36.5	53.6
6	C_2	M	20.2	0.108	0.72	0.22	−5.4 [−5.4]	−83.2	−18.2	45.0
					[16]Annulenes					
7	S_4	H	0.0	0.097[j]	0.76	0.38	+10.9 [+9.4]	−63.9	0.0	32.6
8	C_1	H	2.0	0.105	0.75	0.35	+10.7 [+9.3]	−65.6	−1.7	26.7
9	C_1	M	5.1	0.087	0.84	0.57	−6.3 [−4.6]	−110.0	−46.1	52.5
10	C_2	M	7.6	0.097	0.80	0.48	−3.9 [−3.4]	−103.7	−39.8	47.1
11	C_2	M	15.8	0.019	0.997	0.93	−14.5 [−14.4]	−176.8	−112.9	29.1
12	C_2	M	51.4	0.051	0.94	0.81	−15.6 [−11.5]	−144.6	−80.7	73.1
					[20]Annulenes					
13	C_1	H	0.0	0.095	0.81	0.50	+12.1 [+10.9]	−75.6	0.0	29.5
14	C_2	M	6.2	0.049	0.95	0.85	−10.2 [−9.3]	−170.8	−95.2	29.9
15	C_2	M	10.0	0.086	0.85	0.62	−4.2 [−3.7]	−131.4	−55.8	41.9
16	C_2	M	23.5	0.065	0.91	0.75	−9.8 [−7.7]	−149.7	−48.5	30.9

[a] H = Hückel topology, M = Möbius topology. See ref 13 for definitions. [b] Zero point-corrected B3LYP/6-31G* relative energies. Vibrational analyses confirmed all species to be minima. The absolute energies (au) of the reference species are **1**, −464.37912; **7**, −619.21450; and **13**, −774.03316. [c] Differences, in Å, between the shortest and longest C−C bonds. [d] Julg parameter *A*. [e] HOMA indexes. [f] NICS(0) was computed (GIAO/B3LYP/6-31+G*//B3LYP/6-31G*) at the ring centers and NICS(1) 1.0 Å away from the approximate plane of the rings. [g] CSGT magnetic susceptibilities, in cgs-ppm at RHF/6-31+G*. [h] Magnetic susceptibility exaltations, in cgs-ppm; all [12]annulenes are relative to species **1**, all [16]annulenes to **7**, and all [20]annulenes to **13**. [i] Largest deviation (in deg) of the CCCC dihedral angles from either 0° or 180°. [j] Compare ΔCC = 0.158 Å from ref 19.



7 (S_4) **8** (C_1) **9** (C_1) **10** (C_2) **11** (C_2) **12** (C_2)

Figure 3. B3LYP/6-31G* optimized geometries of [16]annulene isomers. CC bond lengths in angstroms.

have Hückel topologies, i.e., with zero or an even number of sign inversions in the π system.[13] Our attempts to locate Möbius isomers of [12]annulene led to additional minima with surprising features.

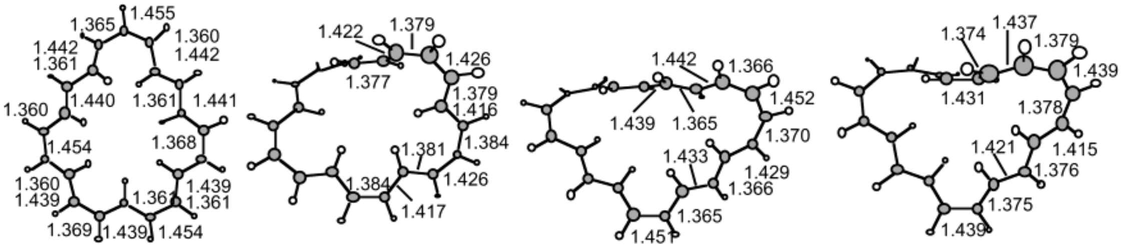
Consistent with Oth's proposed equilibrium, we find the energy of **2** to be only 3.8 kcal/mol higher than that of **1** (Table 1). Interestingly, **3**, with two half−twists and thus a Hückel topology,[13] is predicted to be the most stable [12]-annulene, 0.3 kcal/mol lower in energy than **1**. Compound **4** (neither Hückel nor Möbius) is only 2.5 kcal/mol higher in energy than **1** and is slightly more stable than **2**. Of our two Möbius [12]annulene isomers, **5** is far more stable than **6** and lies only 4.4 kcal/mol above **1**. While these results are consistent with Oth's assignments, they also invite considerations of the possibility that isomers **3**, **4**, and **5** are responsible for some of his experimental observations.

In general, the degree of bond-length alternation (ΔCC) in these systems parallels the dihedral angle deviations from ideality (∠CCCC in Table 1). Species **1**−**4** and **6** follow this pattern well. The exception is Möbius isomer **5**; despite its rather large CCCC dihedral angle of 53.6°, **5** has the smallest degree of bond-length alternation as well as the largest Julg parameter (0.90) and HOMA index (0.69) of the set.

NICS shows **1** to have a paramagnetic ring current, in agreement with the experimental NMR data. The small negative NICS value computed for **2** is likely due to local effects.[4b,18] The negative NICS of **3** (−8.1) seems to indicate aromaticity but is due to the local contributions of radially oriented π-orbitals.[18] In agreement with the geometric results, the magnetic properties of **5** also show it to be the most

---

(18) Martin, N. H.; Brown, J. D.; Nance, K. H.; Schaefer, H. F.; Schleyer, P. v. R.; Wang, Z.-X.; Woodcock, H. L. *Org. Lett.* **2001**, *3*, 3823.



13 (C_1) **14** (C_2) **15** (C_2) **16** (C_2)

Figure 4. B3LYP/6-31G* optimized geometries of [20]annulene isomers. CC bond lengths in angstroms.

aromatic of all of the [12]annulenes studied here: **5** has the largest negative values both for NICS(0) (−14.6) and for NICS(1) (−12.7). The large MSE (−36.5) also documents the presence of a diamagnetic ring current. The remaining species, **4** and **6**, do not show strong evidence of aromaticity.

Thus, we have located a Möbius [12]annulene isomer, **5**, that is predicted to possess substantial aromatic character and to be only 4.4 kcal/mol higher in energy than the previously reported Hückel isomer **1**. The higher energy of **5** relative to **1** is due to angle strain: the CCC bond angle average is 130.2° in **5**, compared to 125.3° in **1** and the ideal value of 124.3° in acyclic polyenes.

[16]Annulenes. The two [16]annulene isomers shown at the top of Figure 3 are known experimentally. The crystal structure of S_4-symmetric **7** has been reported,[19] while NMR studies suggest that both **7** and the less stable **8** are in equilibrium in solution.[20] Indeed, **7** and **8** are computed to be the two lowest energy [16]annulenes in Table 1; **8** is only 2 kcal/mol less stable than **7**. However, both have Hückel topologies and sizable positive NICS values, indicating paratropic ring currents (antiaromaticity).

The remaining [16]annulene entries all have Möbius topologies and show varying degrees of aromatic character. The most striking example of a neutral Möbius aromatic system, **11**, has nearly perfect bond length equalization (both the Julg parameter and the HOMA index approach 1), a NICS value of −14.5 ppm (see graphical abstract), and a huge MSE of ca. −113 cgs-ppm relative to **7**. The other three Möbius isomers are less aromatic than **11**. There is good agreement among the various magnetic and geometric criteria; Julg and HOMA values decrease (i.e., as bond-length alternation becomes more pronounced) along with the decrease of the NICS and MSE values.

The relative energies, however, do not agree well with the degree of aromaticity based on these criteria. The most aromatic Möbius [16]annulene, **11**, is over 10 kcal/mol higher in energy than **9**, the most stable Möbius isomer. Clearly aromatic stabilization is not great enough to overcome the strain associated with the different conformations. In 1991, Hernando and co-workers found that “valence angle strain” determined the relative AM1 stabilities of the known [16]-annulenes.[21]

[20]Annulenes. In his landmark paper, Heilbronner suggested that annulenes with 20 or more carbons should be able to accommodate a Möbius twist “without introducing any apparent bond angle or steric repulsion strain.”[1a] Sondheimer and Metcalf synthesized [20]annulene in 1971; ^{1}H NMR data showed a paramagnetic ring current and a mixture of stereoisomers, one of which was **13** (Figure 4).[22] While finding **13** to be the most stable [20]annulene isomer (Table 1), we also located three Möbius isomers (**14−16**). The best one, **14**, is only 6.2 kcal/mol higher in energy than **13** and exhibits significant aromatic character (Table 1). The relative energies of **13−16** correlate with the average deviations of the CCC angles from the strain-free 124.3° value.[21] In accord with Heilbronner’s expectation, **14** has the least amount of angle strain and (with the exception of **11**) the greatest degree of bond-length equalization of all the Möbius annulenes reported here.

In summary, we have predicted several Möbius local minima of [12]-, [16]-, and [20]annulene. Strong evidence for aromaticity is computed for **5**, **11**, and **14,** in particular. However, because of counterbalancing strain effects, the most stable isomers in all three sets have Hückel topologies. Nevertheless, Möbius isomers may play a role in the chemistry of [4*n*]annulenes. Experimental investigations are currently underway.

Acknowledgment. We dedicate this paper to Professor Edgar Heilbronner. C.C. and W.L.K. are grateful to the Lily Drake Cancer Research Fund and the University of San Francisco Faculty Development Fund for generous financial support. The Fonds der Chemischen Industrie at Erlangen and the University of Georgia also funded the project. We thank Valentin Gogonea and Ralph Puchta for computational contributions and their interest.

Supporting Information Available: B3LYP/6-31G* optimized Cartesian coordinates for all species, absolute and zero-point energies, NICS values, and magnetic susceptibilities. This material is available free of charge via the Internet at http://pubs.acs.org.

OL026610G

---

[19] Johnson, S. M.; Paul, I. C. *J. Chem. Soc. B* **1970**, 643.

[20] Oth, J. F. M.; Gilles, J.-M. *Tetrahedron Lett.* **1968**, 6259. See also: Stevenson, C. D.; Kurth, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 722.

[21] Hernando, J. M.; Quirante, J. J.; Enríquez, F. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1. They considered the ideal CCC angle to be 120°; we employ 124.3° (the calculated CCC angle for polyenes) in the present work.

[22] Metcalf, B. W.; Sondheimer, F. *J. Am. Chem. Soc.* **1971**, *93*, 6675.