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Racemization Barriers of Helicenes: A Computational Study[1]

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Abstract: The racemization barriers of pentahelicene up to nonahelicene have been computed with AM1, MNDO, and PM3. All methods lead to C_s transition states which have lower energy than those with C_{2v} symmetry. The barriers calculated by AM1 match the experimental values best for all helicenes. The reliability of the results has been confirmed by ab initio methods using the B3LYP functional with the 3-21G basis set as implemented in the GAUSSIAN94 package. Furthermore, 12 methyl-substituted helicenes have been computed with the AM1 method. The racemization barriers of 1-methyl-substituted penta- and hexahelicene are at least as high as that of the next higher unsubstituted helicene. A second methyl group in the 1′-position increases the barrier further, while methyl groups in the 2-position do not have a severe influence on the racemization barrier.

Introduction

Helicenes have gained great attention in the sixties and seventies because of their unique properties. Unsubstituted carbohelicenes are C_2-symmetric species having helical structures and a strong inherent chiral chromophor which exhibits very high specific optical rotations depending on gross structure, fine geometry, electronic interactions, etc.[2−6] Especially the C_2-symmetry and large spatial requirement implies the use of substituted helicenes as chiral auxiliaries or catalysts. Although there are several applications of related C_2-symmetric binaphthyl derivatives in organic synthesis,[7] to the best of our knowledge, only one example of an intermolecular type of enantio direction is known for helicenes.[8] Moreover, crown ethers modified by helicenes have been used for deracemization.[9] The crucial point in this context is the stability of the configuration of helicenes. The lower members of the homologous series are known to racemize quite easily. The small barriers of racemization were interpreted as a result of a non-aromatic bridged helicene[10] as an intermediate state or as two subsequent intramolecular thermic Diels−Alder reactions.[11] Later Martin established that during racemization of one-sided deuterated helicenes no H/D exchange occurs between the two ends of the molecule.[11] Therefore only twisting distributed over a large number of aromatic bonds of the helicenes enables the racemization.

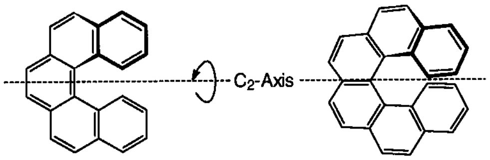

Figure 1. Symmetry of [5]helicene and [6]helicene in the ground state.

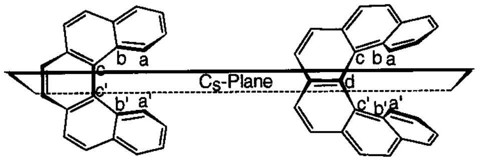

Figure 2. Symmetry of helicenes in the transition state.

For the application of helicenes as chiral auxiliaries or catalysts it is absolutely necessary to employ substances which do not racemize under the usual reaction conditions. As part of our synthetic strategy[13] we estimated the racemization enthalpies of several phenanthrene-benzologous compounds using different semiempirical methods.[14−16]

In the ground state unsubstituted helicenes possess C_2 symmetry (Figure 1). C_s symmetry is expected[12,17] for the transition state of racemization. This geometry was first calculated by Lindner for hexa- and heptahelicene, while a planar C_{2v} symmetry was found for pentahelicene using the π-SCF method[12] (Figure 2).

In the transition state the C_s plane is perpendicular to the plane of the central aromatic nuclei. Because of the symmetry

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(1) Taken in a part from the planned dissertation of R. Janke, Universität Münster.

(2) Martin, R. H. *Angew. Chem.* **1974**, *86*, 727−738; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649−660.

(3) Mallory, F. B.; Mallory, C. W. *Org. React.* **1983**, *30*, 1−456.

(4) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63−130.

(5) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1−76.

(6) Vögtle, F. *Reizvolle Moleküle der organischen Chemie*; B. G. Teubner: Stuttgart, 1989; pp 183−208.

(7) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503−517.

(8) (a) Hassine, B. B.; Gorsane, M.; Geerts-Evrard, F.; Pecher, J.; Martin, R. H.; Castelet, D. *Bull. Soc. Chim. Belg.* **1986**, *95*, 547−556. (b) Hassine, B. B.; Gorsane, M.; Pecher, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1986**, *95*, 557−566.

(9) (a) Nakazaki, M.; Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1983**, *787*−788. (b) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271−276.

(10) Goedicke, C.; Stegemeyer, H. *Tetrahedron Lett.* **1970**, 937−940.

(11) Martin, R. H.; Marchant, M.-J. *Tetrahedron* **1974**, *30*, 347−349.

(12) Lindner, H. J. *Tetrahedron* **1975**, *31*, 281−284.

(13) (a) Janke, R. Diploma Thesis, Münster, 1993. (b) Janke, R.; Haufe, G. *Zh. Org. Khim.* **1994**, *30*, 1365−1367.

(14) Borkent, J. H *E.C.C.C.1 Computational Chemistry*; AIP Conference Proceedings 330; Nancy, France, May 1994, Bernardi, F., Rivail, J.-L., Eds.; p 207.

(15) Borkent, J. H. *First Electronic Computational Chemistry Conference*, paper 27, Nothern Illinois University, November 1994. Proceedings, Published on CD-ROM by ARInternet Corp.: Landover, MD, as ARI CD-101.

(16) Janke, R.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *25. GDCh-Hauptversammlung*; Münster, September 1995; Abstracts of papers, p 443.

(17) Yamada, K.-I.; Nakagawa, H.; Kawazura, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2429−2432.

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Table 1. Comparison of Experimental and Computed Activation Barriers for Racemization (AM1, PM3, MNDO, and π-SCF)

	experimental results			AM1, heat of formation (kcal/mol)			PM3, heat of formation (kcal/mol)			MNDO, heat of formation (kcal/mol)			π-SCF[12] (kcal/mol)
helicene	$\Delta\Delta G$ [kcal mol^{-1}]	$\Delta\Delta S$ [cal mol^{-1} K^{-1}]	$\Delta\Delta H$ [kcal mol^{-1}]	GS	TS	TS-GS	GS	TS	TS-GS	GS	TS	TS-GS	TS-GS [kcal mol^{-1}]
1	24.1[28] (293 K)	-4.1	22.9	104.5	127.4	22.9	99.3	117.9	18.6	101.4	122.8	21.4	24.0[a]
2	36.2[11, 29] (300 K)	-4.2	35.0	126.8	158.2	31.4	120.5	147.6	27.1	123.3	151.6	28.3	36.0
3	41.7[11] (300 K)	-3.9	40.5	151.1	185.8	34.7	142.7	174.4	31.7	146.0	177.0	31.0	41.0
4	42.4[11] (300 K)	-4.6	41.0	175.9	210.8	34.9	165.5	197.3	31.8	168.9	199.6	30.7	
5	43.5[11] (300 K)	-6.1	41.7	200.6	234.6	34.0	188.0	217.8	29.8	181.9	222.5	30.6	

[a] Planar form.

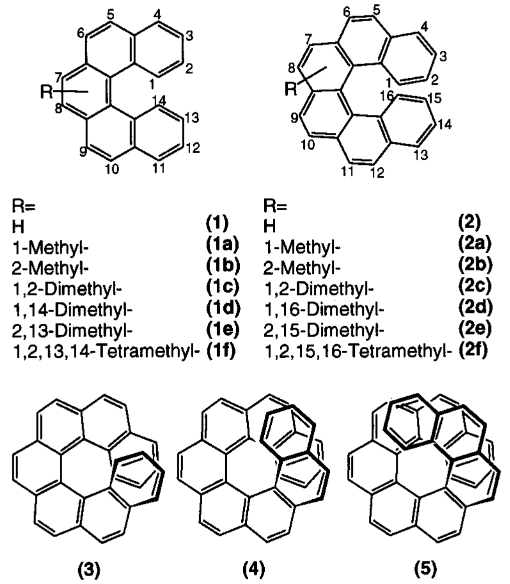

Figure 3. List of the computed helicenes.

in these molecules the twist angles a−b−b′−a′ and b−c−c′−b′ should amount to 0° in the transition state.

Regarding the existing synthetic methods for pentahelicenes, suitable substituted analogues may represent an interesting group of chiral auxiliaries. Unfortunately, for such compounds only few experimental thermodynamic data are available. Therefore we applied three computational methods to estimate their racemization enthalpies. In detail we were looking for effects of the position of additional substituents.

Experimental Section

Three semiempirical methods, AM1,[18,19] MNDO,[20] and PM3,[21] as implemented in the AMPAC 4.5/5.0[22] and MOPAC 7[23] programs, have been used. Full transition structure optimizations have been done using the eigenvector following routine (keyword EF) with symmetry constraints and verified by the transition state routine (keyword TS) without any symmetry constraints. Second derivative (frequency) calculations established the nature of stationary points (with the keyword FORCE). The ab initio calculations were carried out using the 3-21G basis set of the GAUSSIAN94 package of programs[24] for the B3LYP//AM1[25,26] single point calculations and geometry optimization. The Becke3 functional was used for exchange energies and the Lee, Yang, Parr (LYP) functional for the correlation energies. Computations were run on an IBM RS6000-cluster (Münster) and a Silicon Graphics Indigo workstation (Nijmegen).

Results and Discussion

Unsubstituted Helicenes. Calculated (AM1, MNDO, PM3) racemization enthalpies of unsubstituted helicenes are compared with the experimental energies in Table 1.

Several methods were used to locate the C_s transition state structure. These include successive decrease of torsions like b−c−c′−b′ or a−b−b′−a′, adding symmetry constraints to the input Z-matrices, and finally optimization using the TS (eigenvector following) routine as implemented in MOPAC and AMPAC.

In all but one case (nonahelicene, **5**) the C_s structure turns out to be the transition state for racemization. FORCE calculations confirm the structure as a saddle point with only one negative eigenvalue. Minimization of structures with slightly distorted symmetry leads to either of the two helical forms.

The IRC method, as implemented in AMPAC, was used to generate a series of structures along the racemization path for hexa- (**2**),[14,15] octahelicene (**4**) (Figure 4), and nonahelicene (**5**) in order to analyze the conformational changes involved in this process.

Nonahelicene (**5**) makes an exception, in the sense that although the C_s structure is a saddle point, it is not the highest point on the reaction coordinate (Figure 5). Minimization of this structure ends in a conformation with slightly distorted symmetry (Figure 5, local minima, LM1 and LM2). By varying the central dihedral angles, as mentioned above for **2**, an asymmetric saddle point is found (Figure 6), which was characterized as a transition state with the lowest energy (one of the two enantiomeric forms) for racemization (Figure 5, transition states TS1 and TS2).

The reaction path shown in Figure 5 is confirmed by IRC calculations starting from the enantiomeric transition states (TS1 and TS2). Surprisingly large deviations of the twist angles (like a−b−b′−a′) are possible within 1 kcal/mol.

The differences between zero-point energies of ground and transition states, calculated by the FORCE method, are smaller

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(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(19) Herndon, W. C.; Nowak, P. C.; Connor, D. A.; Lin, P. *J. Am. Chem. Soc.* **1992**, *114*, 41−47.

(20) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907.

(21) Stewart, J. P. *J. Comp. Chem.* **1989**, *10*, 209−220.

(22) AMPAC 4.5/5.0, 1994 Semichem, 7128 Summit, Shawneee, KS 66126.

(23) MOPAC 7.0, Quantum Chemical Program Exchange (455), Indiana University, Bloomington, Indiana.

(24) Gaussian 94 (Revision A.1), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Chesseman, J. R.; Keith, T. A.; 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, W.; Andres, J. L.; Replogle, E. S.; Comperts, R.; Martin, R. L.; Fox D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A.; Gaussian, Inc.: Pittburgh, PA, 1995.

(25) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(26) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336−10337.

(27) Visualization by Rasmol 2.4, Copyright (C) 1992, 1993,1994 by Roger Sayle.

(28) Goedicke, C.; Stegemeyer, H. *Tetrahedron Lett.* **1970**, 937−940.

(29) Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* **1972**, 3707−3708.

Table 2. Comparison of Experimental, AM1, and ab Initio B3LYP/3-21G Results for the Activation Barriers of Racemization

		AM1			B3LYP/3-21G	
helicene	$\Delta\Delta H^a$ [kcal mol^{-1}]	GS^b [kcal mol^{-1}]	TS^b [kcal mol^{-1}]	TS-GS [kcal mol^{-1}]	TS-GS^c [kcal mol^{-1}]	TS-GS^d [kcal mol^{-1}]
1	22.9[28]	104.5	127.4	22.9	28.02	25.65
2	35.0[11,29]	126.8	158.2	31.4	40.50	38.16
3	40.5[11]	151.1	185.8	34.7	44.31	42.04
4	41.0[11]	175.9	210.8	34.9	43.38	41.76
5	41.7[11]	200.6	234.6	34.0	40.80	39.72

[a] Experimental results. [b] Heat of formation. [c] B3LYP/3-21G//AM1. [d] B3LYP/3-21G//B3LYP/3-21G.

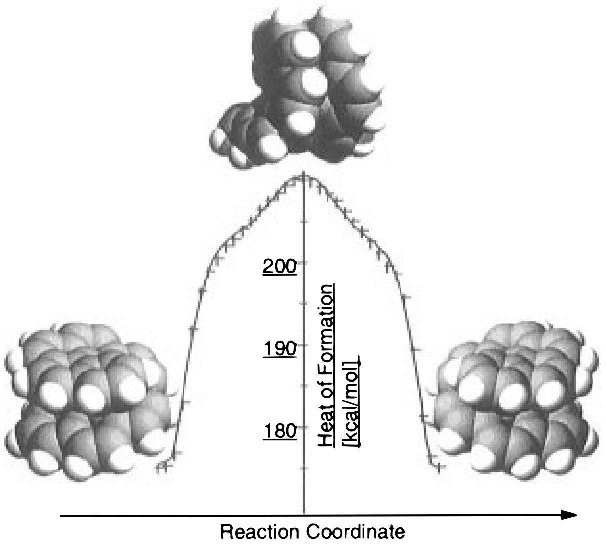

Figure 4. AM1-racemization path of octahelicene (**4**) computed with the IRC method of AMPAC. (CPK model by RasMol[27]).

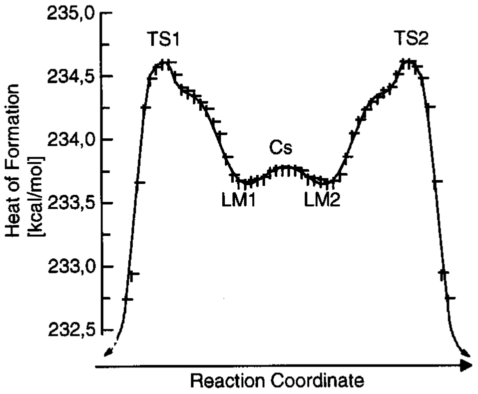

Figure 5. Detail of the racemization path of nonahelicene (**5**).

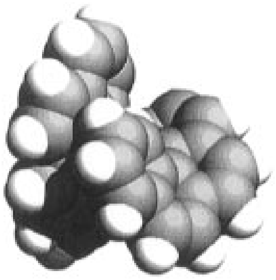

Figure 6. CPK model of one of the enantiomeric transition states (TS*n*, with *n* = 1,2) of nonahelicene (**5**).

than 0.6 kcal/mol for all helicenes. Therefore the zero-point energy corrections were not taken into account.

The comparison of the calculated racemization energies and experimental values shows the best correspondence for the AM1 results (Figure 7); MNDO and PM3 exhibit considerable deviations. For larger helicenes all methods show substantial differences to the experimental values.

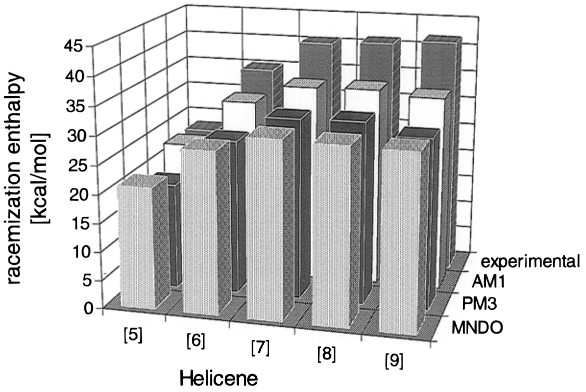

Figure 7. Racemization enthalpies of unsubstituted helicenes.

In agreement with the experiment the calculations indicate that the racemization barriers for octahelicene (**4**) and for the higher homologues have no substantial differences. Unexpectedly, the computed racemization barriers decrease for octahelicene (**4**) (MNDO) or nonahelicene (**5**) (AM1, MNDO, and PM3). Extra rings added formally to the almost parallel terminal rings in the C_s structure of the [7]helicene (**3**) point freely in space. Therefore they introduce less steric energy in the transition state than formal adding of the same rings into the helical structure of the ground state. At least it is not possible to give a conclusive interpretation for the increasing experimental racemization barriers of the higher helicenes.

Subsequent to the semiempirical computations we tested their reliability with ab initio calculations. We used the ground states and the C_s-symmetric transition states of the AM1 optimizations for single-point calculations using the B3LYP functional and the 3-21G basis. The calculated racemization barriers were higher for all examined helicenes compared to the AM1 method and higher than the experimental values for almost all helicenes, too. Only in the case of nonahelicene (**5**) was the ab initio enthalpy lower than the experimental value.

The optimization of these geometries with GAUSSIAN94 reduced the racemization barrier in all cases for some kilocalories per mole (Table 2). For nonahelicene (**5**) we started the optimizations with the C_s- as well as the C_1-symmetrical transition state. Both computations lead to the C_s transition state. In correspondence to our semiempirical results the racemization barrier is decreasing for octahelicene (**4**) as well as for nonahelicene (**5**).

For the higher helicenes **3**, **4**, and **5** the ab initio results give values for the racemization enthalpies which are closer to the experimental ones in comparison to the AM1 calculations. For hexahelicene (**2**) the ab initio barrier is considerably too high. At least the match of the pentahelicene racemization of AM1 cannot be improved by any other method.

Methyl-Substituted Helicenes. Methyl substituents at the terminal rings of the helicene skeleton have a major influence

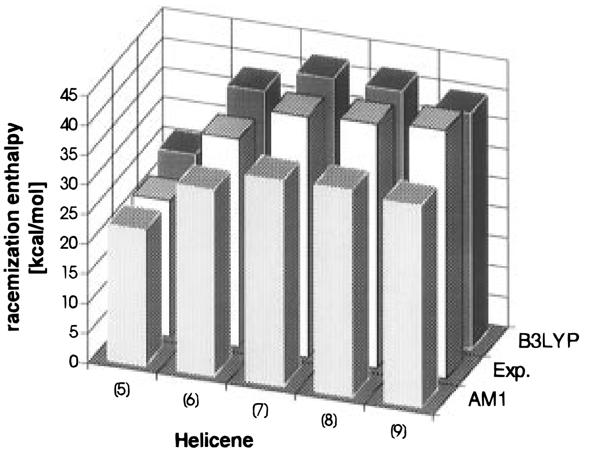

Figure 8. Comparison of AM1 and ab initio calculated racemization enthalpies of unsubstituted helicenes.

Table 3. Comparison of Experimental X-ray Pitches [Å] of Helicenes[5,35]

helicene	inner	middle	outer
2	3.26	4.58	6.04
3	3.16	3.86	4.41
[10]helicene	3.22	3.65	3.88
[11]helicene	3.23	3.64	3.93
2d	3.24	3.94	4.02

on the structure of the ground state[5,9b,30,31] as well as on the racemization barriers.[5,32−34]

The structure of helicenes can be described generally in a simple way[35] by distributing the atoms of the skeleton on three screw lines: one inner helix having n + 1 carbon atoms, one outer helix being composed of 2n carbon atoms, and one middle helix containing again $n + 1$ carbon atoms, where n is equal to the number of benzene rings. Generally, the pitch of the inner helix is smaller than that of the middle helix, which is again smaller than that of the outer helix (Table 3).

The examination of the pitches determined by X-ray analysis for several helices shows nearly equal values for the inner helix of all helicenes. The pitches of the middle and outer helix decrease significantly from [6]helicene (**2**) to [11]helicene (Table 3). The 1,16-dimethyl[6]helicene (**2d**) is similar in structure to [10]- or [11]helicene as is shown by a comparison of their pitches.

The calculated AM1 pitches of hexahelicene (**2**) are much smaller compared to the X-ray results, but are larger for all other helicenes (Tables 3 and 4). Analogous to the experimental data the calculated pitches of the middle and the outer helices are decreasing toward unsubstituted higher helicenes. A methyl-substituent in the 1-position of [6]helicene (**2a)** increases the inner, middle, and outer pitch. In 2-position (**2b)** there is no effect of a methyl group substitution. Two methyl groups in the 1- and 2-positions (**2c)** increase the inner pitch, do not affect the middle pitch, but decrease the outer pitch. Two methyl substituents in the 1- and 16-positions (**2d)** increase the inner and middle pitch, but decrease the outer pitch, while methylation in the 2- and 15-positions (**2e)** decreases all pitches (Table 4). X-ray analyses, however, show that additional methyl groups lead to smaller pitches of all helices in **2d** (Table 3)[5]. Force-field calculations by Laarhoven et al.[36] generally gave smaller differences between X-ray structures and computed results.

Table 4. Comparison of Pitches [Å] of Computed Helicenes (AM1-Calculations)

helicene	inner	middle	outer
2	3.11	4.32	4.86 (C−H)
3	3.35	4.33	5.20
4	3.61	4.37	4.82; 4.71
5	3.61	4.13	4.37
[10]helicene	3.65	3.93	4.12; 4.24
[11]helicene	3.67	3.89	3.98
2a	3.34	4.39	5.13 (C−H)
2b	3.11	4.33	4.87 (C−H)
2c	3.32	4.30	4.46 (C−H)
2d	3.58	4.44	4.81 (C−H)
2e	3.01	4.16	4.65 (C−CH_3)

Table 5. Calculated Heats of Formation of Methyl-Substituted Helicenes in Comparison to Experimental Results

	experimental results			AM1, heat of formation (kcal/mol)		
helicene	$\Delta\Delta G$ [kcal mol^{-1}]	$\Delta\Delta S$ [cal mol^{-1} K^{-1}]	$\Delta\Delta H$ [kcal mol^{-1}]	GS	TS	TS-GS
1a	38.7[34] (473 K)			102.8	134.5	31.7
1b				95.9	119.8	23.9
1c				96.2	127.9	31.7
1d				102.7	140.1	37.4
1e				88.3	112.1	23.8
1f				89.6	126.3	36.7
2a	43.8[32] (542 K)	-9.8	38.5	126.8	159.3	32.5
2b				119.2	141.1	31.9
2c				121.2	153.6	32.4
2d	44.0[32] (543 K)			127.1	161.7	34.6
2e	39.5[32] (513 K)			111.7	144.3	32.6
2f				115.7	149.6	33.9

In comparison with the unsubstituted helicenes **1**−**5** the experimental racemization entropy $\Delta\Delta S$ of 1-methyl[6]helicene (**2a**) shows that the entropic part of the racemization Gibbs energy $\Delta\Delta G$ is increasing with methyl substitution. Therefore, the Gibbs energy of the methyl-substituted helicene **2a** is significantly higher than that of the [9]helicene (**5**). In contrast, the experimental racemization enthalpy $\Delta\Delta H$ of **2a** is about 2 kcal mol^{-1} lower than that of the [7]helicene (**3**) and 3.5 kcal mol^{-1} higher than that of [6]helicene (**2**). The calculated enthalpy of **2a** also is 2.2 kcal mol^{-1} lower than that of the computed **3** and 1.1 kcal mol^{-1} higher than that of **2**. This means that the methyl substituent is considered accurately by the AM1 method. Its stabilizing effect in the 1-position is similar to that of an additional aromatic nucleus. This effect can be observed as well in 1-methyl[5]helicene (**1a**). The computed racemization enthalpy is about as high as that for [6]helicene (**2**). A second methyl-group at the other end of the helicene (1,14-dimethyl[5]helicene (**1d**) or 1,16-dimethyl[6]-helicene (**2d**)) has an additional stabilizing effect on the configuration. Introducing methyl substituents into the 2-position of helicenes as in **1b** or **2b** has no severe effect on the stability of the enantiomers. A second substitution in the 2′-position of the helicene skeleton as in **1e** also has no significant effect. The energetic level of the ground and transition states is mainly determined by the hydrogen and carbon atoms in the 1- and 14-positions, respectively. In 2,15-dimethyl-hexahelicene

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[30] (a) Frim, R.; Zilber, G.; Rabinovitz, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1202−1203. (b) Frim, R.; Goldblum, A.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 267−274.

[31] Brown, A.; Kemp, C. M.; Mason, S. F. *Mol. Phys.* **1971**, *20*, 787−800.

[32] Borkent, J. H.; Laarhoven, W. H. *Tetrahedron*, **1978**, *34*, 2565−2567.

[33] Fritsch, R.; Hartmann, E.; Andert, D.; Mannschreck, A. *Chem. Ber.* **1992**, *125*, 849−855.

[34] Scherübl, H.; Fritzsche, U.; Mannschreck, A. *Chem. Ber.* **1984**, 117, 336−343.

[35] Navaza, J.; Tsoucaris, G.; le Bas, G.; Navaza, A.; de Rango, C. *Bull. Soc. Chim. Belg.* **1979**, *88*, 863−870.

[36] Somers, J. B. M.; Borkent, J. H.; Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 110−114.

(**2e**) the disubstitution has only a small effect. In this case the distance of the methyl substituents is smaller than in **1e**.

These calculations could not quantify the entropy effect caused by the methyl groups in the transition state or other conformations along the racemization coordinate. Such an effect has been postulated by Borkent and Laarhoven[32] to explain the high experimental entropy contribution in the racemization energy. The semiempirical computations however do not give a conclusive answer to this question.[14]

Conclusions

We have shown that semiempirical computations and especially the AM1 method are useful for calculating racemization barriers of helicenes. On this basis it is possible to estimate the conformational stability of any helicene. The application of ab initio methods is very expensive in computer time. It confirms the results in quality, but does not upgrade in quantity. The use of large ab initio basis sets seems to be an application for future computer generations.

The applied methods proved that methyl substituents in the 1-position increase the stability of the configuration significantly. The effect is similar to that of an additional aromatic ring. For synthetic applications of helicenes as chiral auxiliaries or catalysts the introduction of appropriate methyl groups can possibly avoid several consecutive photochemical cyclizations, which are necessary for the synthesis of the higher homologous.[37] Particularly for the syntheses of pentahelicene derivatives non-photocyclization methods are known.[38,39] We conclude from our computations that suitable substituted pentahelicenes should be configurationally stable enough to be used as chiral auxiliaries.

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Supporting Information Available: Full Geometry and Energy information in the form of GAUSSIAN 94 archive entries (5 pages). Ordering information is given on any current masthead page.

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(37) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York and Basel, 1989; Vol. 10, Chapter 2.

(38) Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923−2925.

(39) Stará, I. G.; Stary, I.; Tichy, M.; Závada, J.; Hanuš, V. *J. Am. Chem. Soc.* **1994**, *116*, 5084−5088.