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CONFORMATIONAL STUDIES ON HEXAHELICENES—IV[1]

THE CONFORMATION OF 1,16-DIMETHYLHEXAHELICENE

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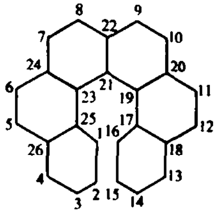
Abstract—From the analysis of NMR data of several mono- and dimethylhexahelicenes it has been concluded that the conformation of hexahelicenes substituted at C(1) or C(3) does not alter when a second substituent is introduced in a non-hindering position (C14) of the other terminal ring.

From the NMR spectrum of 1,16-dimethylhexahelicene and the known structure of hexahelicene it was possible to give a general description of the conformational changes in the helix due to methyl groups in the overcrowded region (C1 and C16). The proposed conformation has been fully substantiated by an X-ray analysis of 1,16-dimethylhexahelicene.

INTRODUCTION

From a previous analysis of NMR spectra of hexahelicenes with alkyl substituents in one of the terminal rings[2] it has been concluded that even large substituents (e.g. t-butyl) at C(2) or C(3) do not alter the geometry of the helix of hexahelicene (1).† The NMR data did not allow to choose between the theoretical model of Herraez[3] in which twisting mainly occurs about the central bonds (C(19)–C(21) and C(21)–C(23)), and the model proposed by Kitaigorodsky[4] in which twisting is smeared out over the whole inner core.



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Meanwhile X-ray analyses of hexahelicene[5] and 2-methylhexahelicene[6] revealed that these compounds have indeed quite similar geometries which appear more like that of Herraez's model.

Starting from this known geometry of **1** introduction of a methyl substituent at C(1) in hexahelicene should lead to strong nonbonding interactions within the molecule. Our previous NMR data of 1-methylhexahelicene (**2**)[2] gave already an experimental evidence for substantial differences between the conformations of **1** and **2**. In that paper we stated that the occurrence of free rotation of the large t-butyl substituent at C(1) at temperatures as low as −80°C is in better agreement with Kitaigorodsky's structure model for 1-substituted hexahelicenes.

The conformational studies have now been extended to 1,16-dimethylhexahelicene (**3**) which has two Me substituents in hindering positions of both terminal rings. For comparison some other new, alkylated hexahelicenes (4-methyl-, 1,14- and 3,14-dimethylhexahelicene) have also been investigated.

RESULTS AND DISCUSSION

(1) *Synthesis.* 4-Methylhexahelicene (**4**) was prepared according to a scheme given previously.[2] The dimethylhexahelicenes were obtained in a single procedure *via* a Wittig reaction with the bis triphenylphosphonium salt of 2,7-bis-(bromomethyl)naphthalene and 2 equivalents of *m*-tolualdehyde (*cf* Ref 7). The resulting product, 2,7-bis-(*m*-methylstyryl)naphthalene (**5**), was irradiated in benzene solution, and the irradiation mixture was separated by column chromatography. The expected products (**3**, **6** and **7**) were isolated in 8, 40 and 30% yield, respectively (Eq 1).

(2) *UV spectra.* In the series of monoalkyl substituted hexahelicenes the UV spectra have been found to be very similar to that of hexahelicene itself.[2] Only with the 1-substituted derivatives a bathochromic shift and/or loss of fine structure of the α and p-bands were found. In Table 2 the wavelengths and log ε values of the maxima in the spectra of the three dimethylhexahelicenes in CH_2Cl_2 are given.

Whereas the data of **7** and **6** are again very similar with those of hexahelicene and 1-methylhexahelicene, respectively, the spectrum of **3**

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†For the discussion of our results we extend the numbering of ring atoms, introduced by Newman, as indicated in the figure.

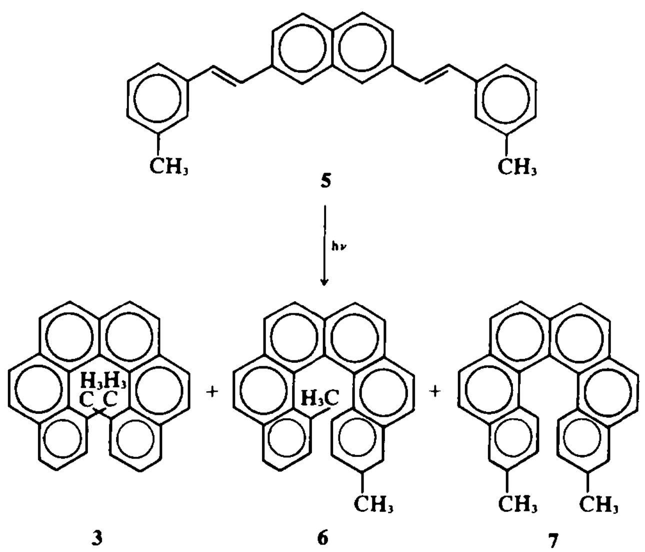

Table 1. λ max (in nm) of substituted hexahelicenes, in CH_2Cl_2; log ε in parentheses; inflections in brackets

Compound	α	p	β
3 1,16-diCH_3	420(2·81); 395(2·93);		[335(4·35)]; 325(4·38); [313(4·23)]
6 1,14-diCH_3	420(2·89); 395(2·97);	[355(4·13)];	326(4·42); [313(4·28)]; [266(4·75)]
7 3,14-diCH_3	405(2·71); 387(2·89);	[350(4·15)];	326(4·48); 315(4.49); [302(4·33)]

shows remarkable differences. The β band has been shifted to longer wavelength, and a p-band cannot be detected, probably due to overlap with the β band. Though the differences are not very pronounced, they point to differences between the helical structure of hexahelicenes with one and with two methyl groups at a hindering position.

(3) *NMR spectra.* The spectra were measured in CS_2 solution with a Varian HA-100 spectrometer; only with 4 a Varian XL-100 apparatus with Fourier transformer was used because of the low solubility of the compound.

Frequencies were determined with the side-band technique. The assignment of peaks was done by decoupling experiments or by comparison with spectra of known, related compounds. For the signals of H(5)–H(12) these methods could not always be used. Therefore the data given in Table 2 for these protons are partially tentative, but the assignment chosen will be explained in the text.

In this Table chemical shifts (in ppm) of all protons of the new compounds (3–7) together with those of 1, 2 and 3-methylhexahelicene (8) are tabulated. In order to get insight into the conformational alterations due to the introduction of Me substituents, the measured δ-values have to be corrected for all other effects of these substituents on chemical shifts of ring protons. Comparison of the spectra of 1 and 3- (or 2-) methylhexahelicene which have quite similar conformations reveals that a β-methyl substituent induces a downfield shift of 0·23 ppm for *ortho* H_α, 0·15 ppm for *ortho* H_β, and 0·10 ppm for *meta* H_α (see also Ref 2). A similar comparison of the spectra of 1 and 4 provides corrections for the influence of an α-methyl substituent: 0·16 ppm for *ortho* H_β, 0·11 ppm for *meta* H_β, and 0·14 ppm for *para* H_α. The rather large downfield shift of H(5) in 4 was expected for steric reasons. In Table 2 corrected δ-values for some relevant protons have been given in parentheses.

Inspection of the NMR data of compounds 7 and 8 reveals that the introduction of two Me substituents (in 7) in nonhindering positions of both terminal rings has as little influence on the conformation as only one such a substituent (in 8). The δ-values of protons (1), (2) and (4), and of the methyl protons are nearly equal in both compounds, and naturally the corrected values of protons (13), (15) and (16) in 7 are equal to the corresponding values of 1. The Me substituents in 7 cause non-equivalence of H(5) and H(6) which is not found in 1,[8,9] but on the whole the positions of the proton signals of the inner rings correspond very well with those of hexahelicene.

A similar comparison of the spectra of 2 and 6 shows again that the introduction of the 14-Me substituent is not accompanied with conformational changes. The δ-values of protons in the 1-substituted ring are equal in both compounds, and the same is true for the protons of the 1-Me group.

Table 2. Chemical shifts (in ppm) of protons in substituted hexahelicenes, measured in CS_2

proton \ substituents	none 1^b	3-CH_3 8^b	4-CH_3 4	1-CH_3 2^b	1,14-diCH_3 6	3,14-diCH_3 7	1,16-diCH_3 3
1	7·47	7·36	7·33	—	—	7·39	—
2	6·53	6·39	6·42	6·45 (6·61)	6·46	6·40	6·25
3	7·08	—	6·92	7·06 (7·17)	7·04	—	6·91
4	7·67	7·45	—	7·58 (7·72)	7·60	7·43	7·48
5	7·77		8·01			7·67	7·71
6			7·84			7·57	
7	7·82		7·86			7·77	$7·97^c$
8							$7·86^c$
9							
10							$7·97^c$
11	7·77		7·79			7·75	7·71
12						7·76	
13	7·67	7·69	7·67	7·63	7·33 (7·56)	7·43 (7·66)	7·48 (7·62)
14	7·08	7·11	7·08	6·97	—	—	6·91 (7·02)
15	6·53	6·57	6·50	6·32	6·14 (6·29)	6·40 (6·55)	6·25 (6·41)
16	7·47	7·50	7·40	6·71	6·60 (6·70)	7·39 (7·49)	—
CH_3	—	2·27	2·70	0·80	0·82 2·18	2·26	0·54

[a] Values in parentheses have been corrected for all influences of the neighbouring methyl substituent except that on the geometry of the helix.

[b] Data from Ref 2.

[c] Tentative assignment, explained in the text.

The corrected δ-values of protons in the other terminal ring of **6** differ slightly, especially for H(13), from those of **2**. It may be noted, however, that the corrections used have been derived from data of compounds with a different conformation, *viz* 2- and 3-methylhexahelicene. The difference between the δ-values of the 14-Me group in **6** (2·18) and the 3-methyl group in **8** (2·27) is also a consequence of the fact that **6** like **2** has a conformation different from that of **8** (and **1**).

Finally the δ-values of the protons in **1**, **2** and **3** will be compared.

In contrast with the Me groups in **4** and **8** which do not alter the δ-values of the protons in the opposite terminal ring, the Me group in **2** causes upfield shifts of these protons. Especially the upfield shift of H(16) is very large. Using the correction factor of the α-Me group a downfield shift is observed, however, for the protons of the substituted ring. According to Haigh[8] the δ-value of the H(1) (and H(16)) proton in hexahelicene depends on two competing effects, *viz* an upfield shift due to a shielding effect of the opposite rings, and a downfield shift due to repulsive Van der Waals' interaction as is also found for bay protons of phenanthrene and other phenes. The introduction of a Me group at the hindering position C(1) as in **2** seems to diminish the steric repulsion of H(16) without a corresponding reduction of the shielding effect of the opposite ring. The upfield shifts of H(15), H(14) and H(13) in **2** suggest that these protons experience even a larger shielding of the opposite ring. These facts can be reasonably explained by the supposition that introduction of CH_3 at C(1) causes a torsion about the C(1)–C(25) and the C(25)–C(23) bonds, which tilts the Me group from the opposite side of the molecule, whereas C(2), C(3) and C(4) move simultaneously in an opposite direction. Such a conformational change should lead indeed to an upfield shift for H(16) because its crowding is relieved and also to upfield shifts for H(13–15) because the distances of these protons to the substituted ring are decreased.

Turning to 1,16-dimethylhexahelicene (**3**) it can be expected that a similar change in conformation as found at one side of the helix in **2** will now be present at both sides of the molecule. Comparison of the δ-values of **3** and **2** reveals that indeed the (corrected) δ-values of the newly substituted ring in **3** are higher whereas those of the opposite ring are lower than in **2**, an effect quite similar as in going from **1** to **2**. Apparently a similar difference in conformation as supposed between **1** and **2** exists between **2** and **3**. Additional torsion over bonds of the inner core at both ends of the helix in the latter compound leads to a more regular screwlike conformation which likes that in the model of Kitaigorodsky.[4] The upfield shift of the methyl protons of **3** in comparison with **2** shows that the overall result of the conformational change leads to a structure in which the crowding of the Me groups has been increased.

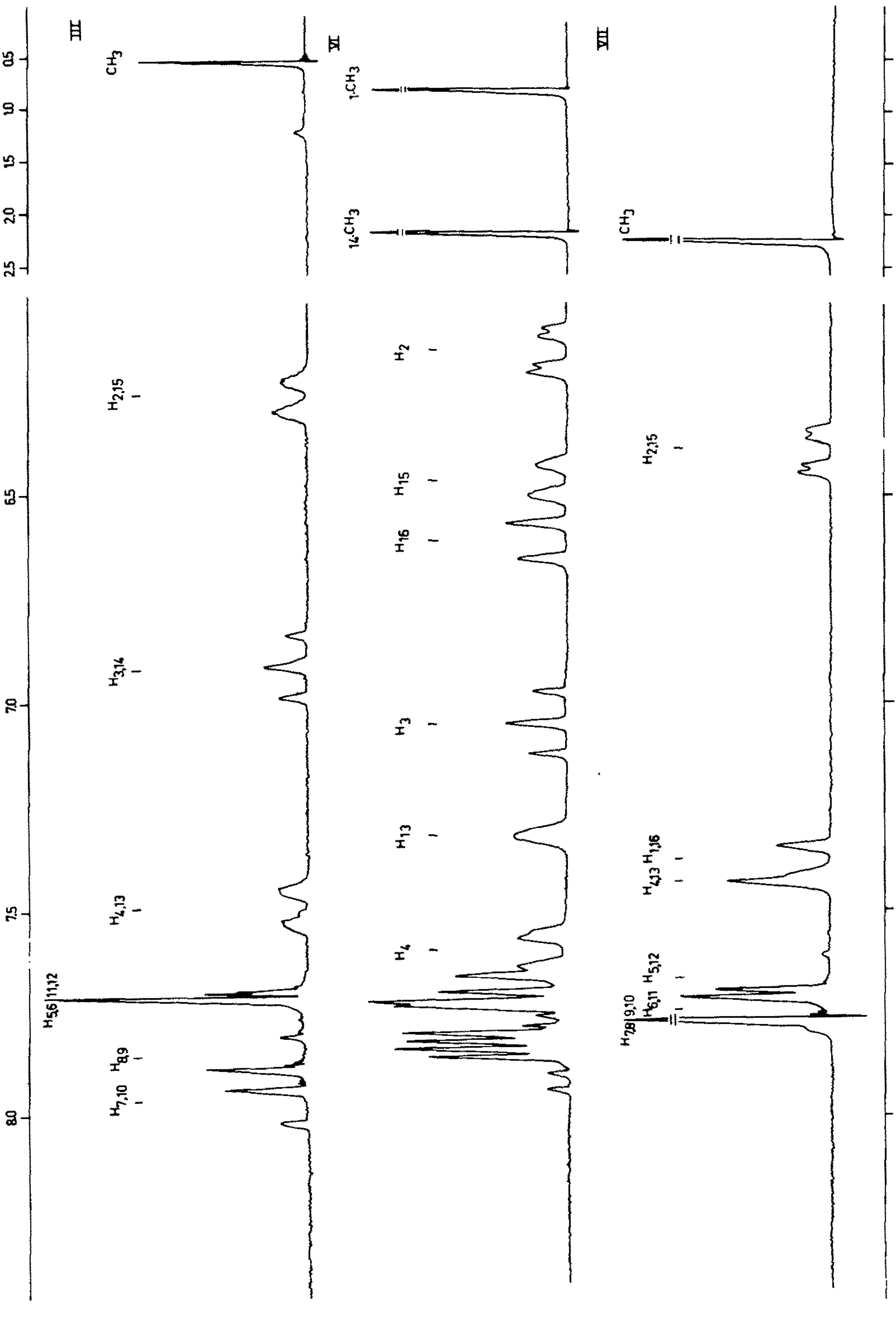

Fig 1. NMR spectra of 1,16-(III), 1,14-(VI) and 3,14-dimethylhexahelicene (VII), measured in CS$_2$ solution.

(4) *X-ray analysis.* To substantiate the conclusions from the NMR data about the conformational changes caused by methyl substituents at C(1) and C(16) an X-ray analysis of **3*** has been made. Anticipating the presentation of all details the structure found is compared with that of **1**[5] in Fig. 2. To this end both molecules have been projected on the least square plane through one of the terminal rings.

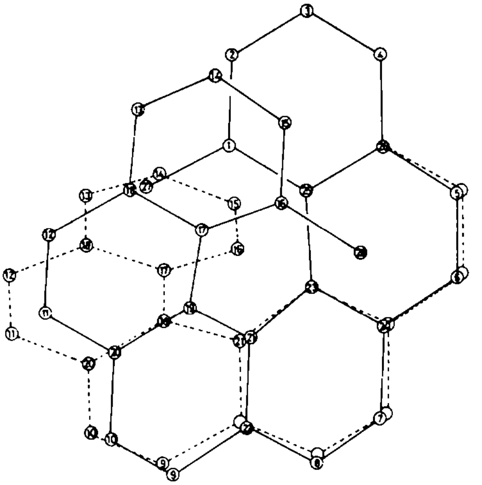

Fig 2. Projection of the carbon atoms of hexahelicene (dotted lines) and 1,16-dimethylhexahelicene on the least square plane through a terminal ring.

In Table 3 same characteristic or critical distances and angles in these molecules and in 2-methylhexahelicene[6] are compared. The most interesting conclusions are:

(a) The screwlike structure of **3** is more regular indeed than that of the other helicenes (see torsional angles); in **1** twisting about inner bonds concerns mainly C(19)–C(21) and C(21)–C(23), but in **3** twisting about C(17)–C(19) and C(23)–C(25) is even larger than that one about the central bonds.

Using the distances and angles found by the X-ray analysis and neglecting possible differences in the ring-currents in **1** and **3** we calculated relative shielding and deshielding values for the protons H(5–8) in **3** from their distances to the least square plane through all six rings with tables of Haigh and Mallion.[10] The values obtained with the assumption of unity of ring current in all rings are H(5) −1·93, H(6) −1·99, H(7) −2·13, H(8) −1·91. They suggest that H(7) will absorb at the lowest field, and that δ-values of H(5) and H(6) will not much differ (Table 2).

Table 3. Characteristic angles and distances in hexahelicene (**1**), 2-methylhexahelicene (**9**) and 1,16-dimethylhexahelicene (**3**)

Torsional angles	1	9	3
C(1)–C(25)	1·5°	2°	14·2°
C(25)–C(23)	11·2°	13°	31·4°
C(23)–C(21)	30·0°	26°	23·0°
C(21)–C(19)	30·3°	30°	23·0°
C(19)–C(17)	15·2°	16°	31·4°
C(17)–C(16)	3·5°	6°	14·2°
Distances			
C(1)–C(16)	3·21 Å	3·16 Å	3·37 Å
C(2)–C(15)	4·58 Å	4·45 Å	4·03 Å
C(3)–C(14)	5·63 Å		4·40 Å
H(1)–C(16)*	3·23 Å		3·75 Å
H(1)–C(17)*	2·67 Å	2·6 Å	2·68 Å
H(1)–C(19)*	2·48 Å	2·5 Å	2·66 Å
Angle between terminal rings	58·5°	54·8°	29·6°

*For **3** H(1) has to be read as that Me proton, which is nearest to the opposite rings.

(b) In **3** the terminal rings are much more parallel, and consequently have much more overlap, than in the other compounds.

(c) The smallest non-bonding C–H distances are between H(1) and C(17) or C(19) in **1** and **9**, and between CH_3 and C(17) or C(19) in **3**. They are in the range from 2·48 Å to 2·68 Å, always smaller than the sum of the Van der Waals' radii (3·0 Å).

The shortest non-bonding carbon-carbon distance, C(1)–C(16), does not vary very much in the compounds, and is again smaller than calculated from Van der Waals' radii (3·6 Å).

(d) The distance between Me (at C(16)) and the least square plane through the terminal ring in **3** is 0·36 Å, indicating that the substituent is bended out of the mean "plane" of the terminal ring over 15°. This rather large value is not exceptional in strained molecules; in paracyclophene an angle of 28° has been found[11] between the methylene group and the mean plane through the benzene ring.

EXPERIMENTAL

The UV spectra were recorded with a Beckman DK2A or a Cary 15 spectrophotometer.

The NMR spectra were measured with a Varian HA-100 or a Varian XL-100 apparatus.

The irradiations were carried out in benzene solutions with iodine added as an oxidant. As a light source four Sylvania blacklite F8T5 lamps surrounding a pyrex tube of 750 ml were used.

Syntheses

2,7-bis(m-methylstyryl) naphthalene (**5**). 2,7-dimethylnaphthalene was brominated with two moles of N-bromosuccinimide. The resulting 2,7-dibromomethylnaphthalene (m.p.: 147°)[12] was transfered into the bis triphenylphosphonium salt by boiling it in xylene with

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*The analysis has been performed by Drs. Th. E. M. van den Hark and Dr. J. H. Noordik (Crystallography Laboratory). Their complete results will be published in *Crystal Structure Communications.*

triphenylphosphine. The phosphonium salt reacted in a Wittig reaction with *m*-tolualdehyde and NaOMe as base into **5** in 75% yield; M.p. *cis–cis*: 150–155°; *cis–trans*: 208–210°; *trans–trans*: 280°.

Irradiation of **5** in a benzenic soln with iodine as an oxidant gave a mixture of the three dimethylhexahelicenes **3**, **6** and **7**. The mixture could partially be separated by column chromatography on silicagel with a mixture of hexane and 10% benzene.

The first fractions contained a mixture of **3** and **6**; they were followed by pure **6** and a mixture of **6** and **7** whereafter pure **7** was eluted. By preparative TLC the unresolved fractions could be separated. Pure products were obtained by crystallization from ethyl acetate.

1,16-*dimethylhexahelicene* (**3**), *yield*: 8%, *m.p.* 259–261°; *UV* (CH_2Cl_2) *max* λ (log ε): 420(2·81); 395(2·93); [335(4·35)]; 325(4·38); [313(4·23)]; 268(4·69); 260(4·73); [253(4·69)]; 237·5(4·67).

1,14-*dimethylhexahelicene* (**6**), yield: 40%, m.p. 185–187°; UV (CH_2Cl_2) max λ (log ε): 420(2·89): 395(2·97); 326(4·42); [313(4·28)]; [266(4·75)]; 259(4·78); [252(4·76)]; 237(4·70).

3,14-*dimethylhexahelicene* (**7**), *yield*: 30%, *m.p.* 253–255°; *UV* (CH_2Cl_2) *max* λ (log ε): 405(2·71); 387(2·89); [350(4·15)];324(4·48); 315(4·49); [302(4·33)]; 257(4·86); 236(4·68).

4-*Methylhexahelicene* (**4**) was prepared by photocyclization of 2-(*o*-methylstyryl)benzo[c]phenanthrene. The latter compound was obtained *via* a Wittig reaction of *o*-tolualdehyde and the triphenylphosphonium salt of 2-bromomethylbenzo[c]phenathrene in 80% yield (m.p. 210–213°). **4** had m.p. 293–295°; UV. (CH_2Cl_2) max λ (log ε): 405(2·53); 385(2·72); [347(4·18)]; 327(4·46); 315(4·48); 303(4·31); 266(4·77); 255(4·79); 208(4·71).

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