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CONFORMATIONAL STUDIES ON HEXAHELICENES—II

SYNTHESIS AND SPECTRAL PROPERTIES OF ALKYL HEXAHELICENES

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Abstract—The synthesis of eight alkyl substituted hexahelicene derivatives by photodehydrocyclization is described.

Analysis of their NMR and UV spectra reveals that the conformation of the helix in hexahelicene is not noticeably disturbed by the introduction of substituents as large as t-butyl or *p*-tolyl at the 2 (or 3) position.

Substitution at C_1, at least with larger substituents (t-Bu) causes bending of the alkyl residue introduced or torsion of the substituted ring. The change in conformation is apparently necessary to alleviate steric crowding.

The results conform better with the hexahelicene model of Kitaigorodsky than with that of Herraez.

INTRODUCTION

SINCE the synthesis of hexahelicene by Newman *et al.*[1] in 1955 a great deal of work has been done on the study of its physicochemical properties (see e.g. Optical Activity: Moscovitz;[2] UV: Weigang;[3] NMR: Martin;[4] Mass Spectrometry: Dougherty;[5] Polarography: Laarhoven).[6]

Though the name of the compound points to a helical structure, the exact conformation has not yet been established by X-ray analysis.* Only two models based on theoretical considerations have been published:

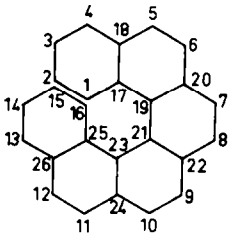
(1) Herraez[8] calculated the minimum potential energy taking into account the non-bonding repulsion energy for interactions between C_1 and C_{16}† and found the following distances from a reference plane (through the bond C_{21}—C_{22}, see formula): C_1 = 1·505 Å, C_2 = 2·06 Å, C_{17} = 1·198 Å.

In this model, the helical structure originates from a large deformation in the two central rings whereas the other rings are rather planar.

(2) Kitaigorodsky[9] used a potential function accounting for non-bonded interactions, angle strain and non-planar distortions. He found for the distances to the same plane of symmetry: C_1 = 1·47 Å, C_2 = 1·94 Å, C_{17} = 0·70 Å.

* During the preparation of the manuscript the determination of the absolute configuration of (−)hexahelicene by X-ray analysis was reported[7] but the paper did not contain data about distances and angles in the molecule.

† In our previous papers we used the IUPAC rules for the nomenclature of the benzohexahelicenes starting with hexahelicene as the parent compound though the latter name is not an official one. For convenience we use in this paper the numbering in hexahelicene as introduced by Newman[1b] and shown in the formula. For the description of the NMR spectra the protons 16–13 of the unsubstituted terminal ring are named A, B, C, D, the protons 1–4 of the substituted ring A′, B′, C′ and D′.



In this model the ring deformations are homogeneously spread over the whole helix. Applied to the 1,16-dimethyl derivative Kitaigorodsky's view led to the conclusion that the helix conformation of this molecule is very similar to that of hexahelicene; critical distances should have the same values in both compounds. An interesting result of the calculations is that the mutual interaction of the Me groups is small in comparison with the repulsion between a Me group and the nearest C atom of the opposite benzene ring (e.g. Me at C_1 and C_{25}).

For an experimental approximation of conformational problems like this careful analysis of NMR spectra has been shown to be very useful (hexahelicene and higher benzologues,[4] benzohexahelicenes[10]).

Knauer[11] used NMR spectra of hexahelicenes for a comparison between experimental and calculated δ-values. His theoretical data were based on the supposition that a bond integral β, differing from zero, between C_1 and C_{16} causes a ring current in the pitch of helical molecules. Using the model of Herraez[8] β was taken as $-0{\cdot}17$. With this value rather good accordance between δ_{calc} and δ_{obs} was obtained. Knauer calculated also the chemical shift of the Me protons in 1-methylhexahelicene, $\delta_{calc} = 0{\cdot}72$. However, the value of $\delta_{obs} = 1{\cdot}72$ seems now to be irrelevant because the identity of the methylhexahelicene used is doubtful.

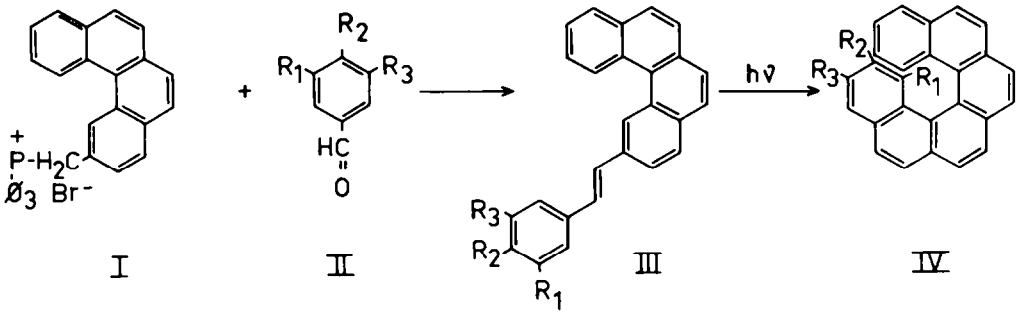
In our investigations NMR analysis has been applied to a larger series of alkyl derivatives of hexahelicene, substituted in a terminal ring. Alkyl substituents were chosen, because their influence on spatial relations could be gradually varied by variations in size (Me, i-Pr, t-Bu) or position (C_3, C_2, C_1) with minimal variations in electronic factors.

Until now only three alkyl derivatives of hexahelicene have been mentioned in literature. Martin[4] used 2-methylhexahelicene for the analysis of the NMR spectrum of hexahelicene but gave no physical data. Dougherty[5] mentioned 7-methylhexahelicene made by Newman. Knauer[11] described a very laborious synthesis of a compound thought to be 1-methylhexahelicene, but his product must have been 2-methylhexahelicene as will be shown in this paper.

RESULTS AND DISCUSSION

(1) *Synthesis.* All compounds but one (IVh, Table 1) were synthesized according to the given scheme. A Wittig synthesis of an appropriate substituted benzaldehyde (II) with the triphenylphosphonium salt of 2-bromomethylbenzo[*c*]phenanthrene (I) gives in 50–90% yield a substituted diarylethylene (III) which on irradiation cyclizes into a hexahelicene derivative (IV). In the case of the 1,3-di-t-Bu derivative starting materials were benzo[*c*]phenanthrene-2-aldehyde and the triphenylphosphonium

salt of 3,5-di-t-butylbenzylbromide. The hexahelicene derivatives were purified by column chromatography and crystallization.



I II III IV

In the photocyclization of the *meta*-substituted phenylbenzo[*c*]phenanthryl ethylene (III, R_1 = Me, R_2 = R_3 = H) both 1-methyl- and 3-methylhexahelicene were formed. The ratio between the compounds was 1:9, as expected in favour of the less hindered 3-Me derivative.

In Table 1, the m.ps of the hexahelicene derivatives are given together with the yield of the photocyclization step and the mass number (M) of the parent peaks.* In the experimental part physical data of the intermediates are given.

TABLE 1. ALKYL DERIVATIVES OF HEXAHELICENE

Substitution	Code	Formula (IV)			Yield[a] in %	m.p. (C°)	M
		R_1	R_2	R_3			
1-methyl	IVa	CH_3	H	H	8[b]	175-176	342
2-methyl	IVb	H	CH_3	H	70	194-198	342
2-i. propyl	IVc	H	i. C_3H_7	H	80	122-123	370
2-t. butyl	IVd	H	t. C_4H_9	H	80	140	384
2-p. tolyl	IVe	H	p. $CH_3C_6H_4$	H	70	164-165	418
3-methyl	IVf	H	H	CH_3	72[b]	186-188	342
1,3-dimethyl	IVg	CH_3	H	CH_3	80	196-198	356
1,3-di-t. butyl	IVh	t. C_4H_9	H	t. C_4H_9	1	221-224	440

[a] Yield of the photocylization step (III → IV)
[b] IVa and IVf are from the same diarylethylene (III)

The product, obtained by Knauer in 0·021% overall yield in a twenty step synthesis starting with 1,8-naphthalic anhydride and assumed to be 1-methylhexahelicene had m.p. 187·5–192°, δ_{CH_3} = 1·73. Both data are in much better agreement with those of 2-methylhexahelicene obtained by our procedure (m.p. 198°, δ_{CH_3} = 1·70). We suppose that in Knauer's procedure a Friedel Craft's cyclization step has been accompanied by migration of the methyl substituent.

* Further data from the mass spectra of the hexahelicenes will be given in a forthcoming paper by Dr F. Gerhartl.

(2) *The NMR spectra.* All NMR spectra were measured in CS_2-solution with a Varian HA100 spectrometer. In contrast to the benzohexahelicenes[10] the spectra of the alkyl derivatives were not concentration dependent (largest differences between 12% and 2% w/v solutions about 2 c/s). Frequencies were measured using the side band technique. By decoupling and tickling experiments the position of the protons of the terminal rings could be estimated. Accurate location of other protons appeared not well possible. As an illustration three spectra have been represented in Fig 1.

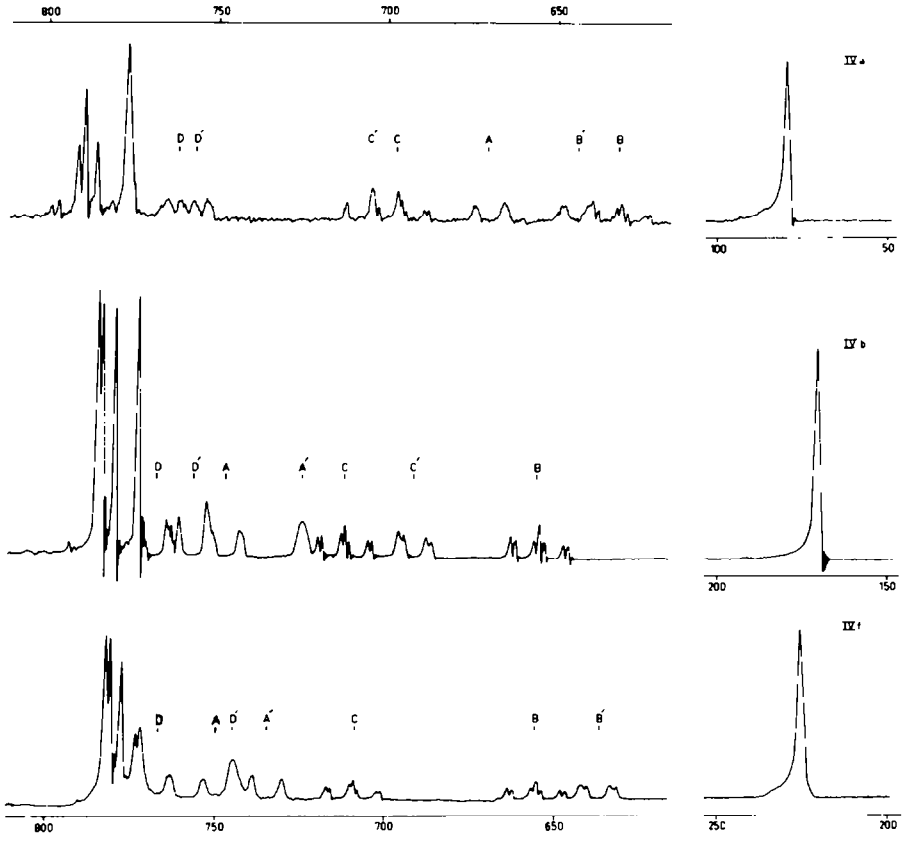


FIG 1. NMR spectra of 1-methyl-(IVa); 2-methyl-(IVb) and 3-methylhexahelicene (IVf) in CS_2 solution (100 Mc/s)

Most of the spectra were recorded also at lower temperatures to detect possible signal splittings caused by steric hindrance in the overcrowded regions. In Table 2, the frequencies of the protons of the substituents are shown together with the differences in shifts (data in parenthesis) at the lowest measured temperature ($-80°$). In Table 3 similar data for the protons on the terminal rings are given.

In Figs 2 and 3 the latter data are plotted. In both figures the frequencies of the hexahelicene protons are added for comparison.

TABLE 2. CHEMICAL SHIFTS (IN PPM) OF THE SUBSTITUENT PROTONS IN ALKYLATED HEXAHELICENES (δ_1) COMPARED WITH THOSE OF ANALOGOUS BENZENE DERIVATIVES (δ_2)

No.	Substitution	Protons concerned	δ_1 (ppm in CS_2)	$(\Delta\delta) - 80^c$ in c/s[a]	Benzene derivatives	δ_2	$\delta_2 - \delta_1$
IVa	1-Methyl	CH_3	0·80 (s)		toluene	2·25	1·45
IVb	2-Methyl	CH_3	1·70 (s)				0·55
IVc	2-i-Propyl	CH_3	0·59 (d)	(−6·5)	i-propylbenzene	1·22	0·63
		CH	2·26 (m)	(+3)		2·82	0·54
IVd	2-t-Butyl	CH_3	0·67 (s)	(−1·8)	t-butylbenzene	1·23	0·56
IVe	2-*p*-Tolyl	*o*-C_6H_4	6·49 (d)	(−14·3)	*p*-ditolyl	7·24	0·75
		m-C_6H_4	6·82 (d)	(−2·3)		7·04	0·22
		CH_3	2·23 (s)			2·28	0·05
IVf	3-Methyl	CH_3	2·27 (s)		toluene	2·25	−0·02
IVg	1,3-Dimethyl	1-CH_3	0·77 (s)	(−7·3)	toluene	2·25	1·48
		3-CH_3	2·25 (s)	(−1·3)	toluene	2·25	0·00
IVh	1,3-Di-t-butyl	1C$(CH_3)_3$	−0·10 (s)	(−12·7)	*t*-butylbenzene	1·23	1·33
		3C$(CH_3)_3$	1·26 (s)	(−7·0)		1·23	−0·03

[a] The values in parenthesis $(\Delta\delta) - 80^c$ are the differences in chemical shift between δ at -80^c and at room temperature

TABLE 3. THE CHEMICAL SHIFTS δ (IN PPM) OF THE PROTONS OF THE TERMINAL RINGS IN HEXAHELICENE DERIVATIVES

	Hexahelicene	2-CH_3 IVb	2-i-C_3H_7 IVc	2-t-C_4H_9 IVd	2-*p*-$C_6H_4CH_3$ IVe	3-CH_3 IVf	1,3-diCH_3 IVg	1-CH_3 IVa	1,3-di-t. C_4H_9 IVh
A	7·47	7·47	7·50 (+0·4)	7·49 (−4·1)	7·61	7·50	6·76 (−2·9)	6·71 (−3·6)	6·43 (−9·0)
B	6·53	6·54	6·56 (+1·0)	6·55 (−0·4)	6·62 (+3·5)	6·57	6·34 (+0·9)	6·32 (−0·6)	6·22 (−0·9)
C	7·07	7·12	7·11 (+2·5)	7·09 (+1·3)	7·11 (+1·5)	7·11	6·98 (−0·1)	6·97 (+0·3)	6·90 (+0·9)
D	7·67	7·67	7·70 (+1·2)	7·68 (+0·3)	7·69	7·69	7·58 (−4·9)	7·63 (0·0)	7·50 (−1·3)
A′		7·23	7·35 (−2·9)	7·54 (−6·7)	7·75	7·36			
B′						6·39	6·30 (−3·6)	6·45 (−2·0)	6·81 (−7·9)
C′		6·91	6·98 (−0·2)	7·16 (−2·5)	7·30 (−11·6)			7·06 (+0·7)	
D′		7·58	7·61 (−1·0)	7·63 (−3·0)	7·74	7·45	7·39 (−3·0)	7·58 (−0·3)	7·47 (−3·9)

The values in parentheses are differences in δ (in c/s) at −80° and at room temperature.

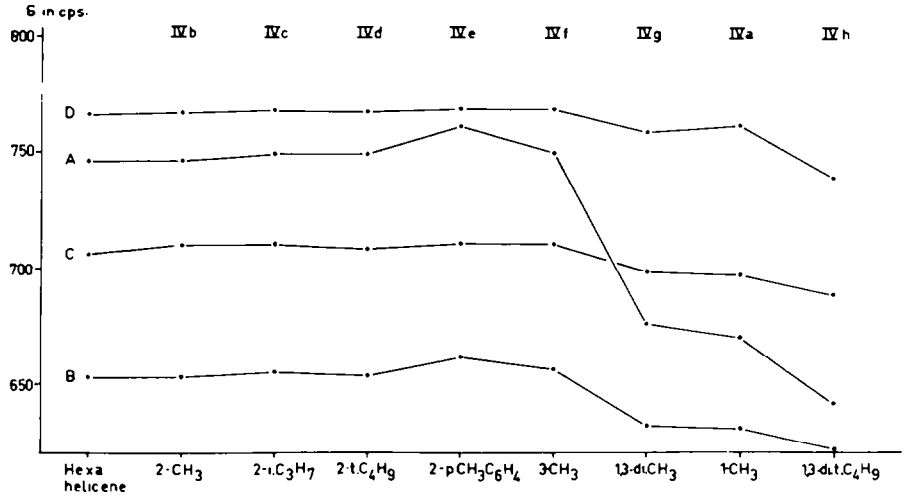


FIG 2. Influence of substituents at positions 1, 2 and 3 of hexahelicene on the chemical shifts of the protons of the unsubstituted terminal ring

From Table 2 it appears that migration of a Me substituent from $C_3 \rightarrow C_2 \rightarrow C_1$ is accompanied by an upfield shift of the Me protons; this effect can be ascribed to an increase in shielding by the opposite ring.

It is striking that the observation that none of the proton signals, including that for the large 1-t-Bu group, is split-up at $-80°$. There is some broadening of the signal of t-Bu at C_1 at this temperature but the same is observed for t-Bu at C_3 though to a lesser degree, and may be caused by increasing viscosity.

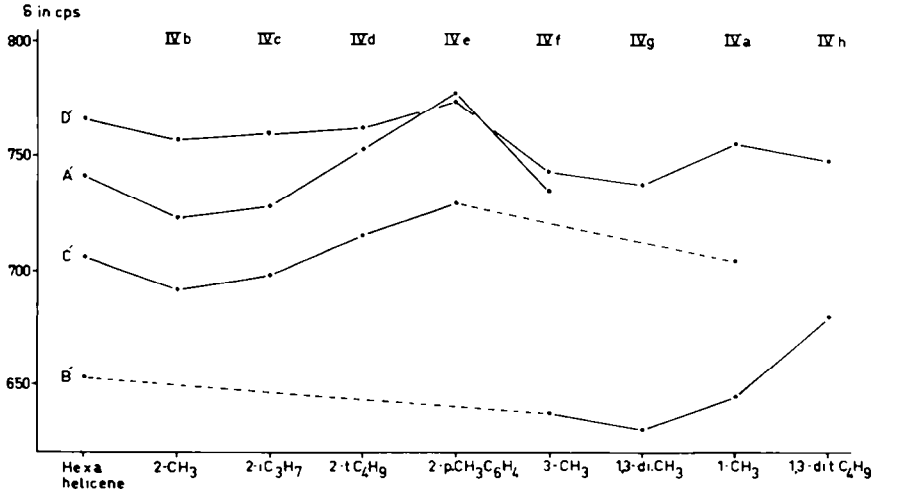


FIG 3. Influence of substituents at positions 1, 2 and 3 of hexahelicene on the chemical shifts of the protons of the substituted terminal ring

It is clear that the serious overcrowding of the 1-substituents by the opposite rings, inherent to the helicene structure, does not lead to hindrance of free rotation even at low temperature.

The differences ($\Delta\delta_{-80°}$, Tables 2 and 3) are small but there are some interesting points:

(1) When the distances between substituent-protons and opposite rings are supposed to decrease, $\Delta\delta_{-80°}$ increases (IVe: *o*H > *m*H; IVg and IVh: 1-CH_3 > 3-CH_3).

(2) The effects in IVc and IVd are peculiar. The Me proton signal of the i-Pr group suffers a larger upfield shift than that of the t-Bu group, and the methine proton of the i-Pr group shifts in the opposite direction. It suggests that the i-Pr substituent in the overcrowded region, although rotating, gets some preference for distinct conformations at lower temperatures. The two diastereotopic CH_3-residues of the i-Pr group have a too small difference in δ to be observed separately. Prof. Martin* showed however, that the signals of the corresponding ^{13}C atoms are distinct ($\delta = +55{\cdot}2$ and $+55{\cdot}5$ ppm from ^{13}C of $CHCl_3$, respectively).

As can be seen from Table 3 and Fig. 2, the effect of a substituent at the 2- or 3-position upon the chemical shift of protons of the opposite ring is very small or negligible. Only in the *p*-tolyl substituted molecule there is a real down-field shift for the A and B protons.

The effect of substituent at the 2- and 3-position is more pronounced for the protons of the substituted ring (Fig 3, Table 3). Compound IVb shows for the *ortho* protons A′ and C′ the normal upfield shift due to substitution when compared with hexahelicene. Structure IVc shows the same effect, although to a lesser degree. The t-Bu and *p*-tolyl substituted molecules (IVd and IVe) show a downfield shift as usual for the *ortho* protons of t-Bu substituted aromatics, and biphenyls.[12]

The large upfield shift for the A protons of the 1-substituted compounds (70–100 c/s compared to hexahelicene) is quite remarkable; for protons B, C and D a similar effect is observable but to a less degree (10–30 c/s).

In the opposite ring the upfield shifts found for the *ortho* and *para* protons B′ and D′ seem to be small in comparison with the effect expected from the substitution; in IVh the very high δ-value of the B′ proton proves quite clearly that another factor must also be of influence in the substituted ring. Several causes may be suggested for these effects:

According to Haigh† the frequency of proton A in hexahelicene is caused by a shielding effect (upfield) and by a steric effect (downfield shift), similar to that on the α_3-, α_4- and α_5-protons in phenanthrene, benzo[*c*]phenanthrene and pentahelicene, respectively.

Studying a molecule mode of 1-t-Bu hexahelicene it is evident that the steric interaction concerns the methyl groups of the t-Bu substituent and the second opposite ring, whereas the A proton experience no longer any steric hindrance. As a consequence the contribution of the steric effect (downfield) on the frequency of A is lost and the position of A is shifted upfield.

Effects of a ring current in the pitch of the helix would be dependent on the value of the bond integral β between C_1 and C_{16}. Knauer showed that above all the δ-values

* Personal communication from Prof. Martin.

† C. W. Haigh, *Mol. Phys.* in press.

of the A-protons are very sensitive for small variations in β. This factor may be visible in the large upfield shifts of the A protons in IVg, IVa and IVh.

It may be that small torsions at one or both ends of the helical chain as a consequence of 1-substitution cause slight changes in ring current effect, resulting in variations in δ-values as found.

All these interpretations have in common that the introduction of alkyl substituents at C_1 should lead to small conformational changes in the helical structure of hexahelicene.

Summarizing it can be stated, that even rather large substituents in position 2 do not disturb the conformation of hexahelicene. This is in agreement with both Herraez' and Kitaigorodsky's models. In these models the distance between C_2 and C_{15} is 4·12 and 3·88 Å, respectively. A substituent at C_2 must be even farther away from C_{15}. So, there must be space enough for free rotating groups in this position.

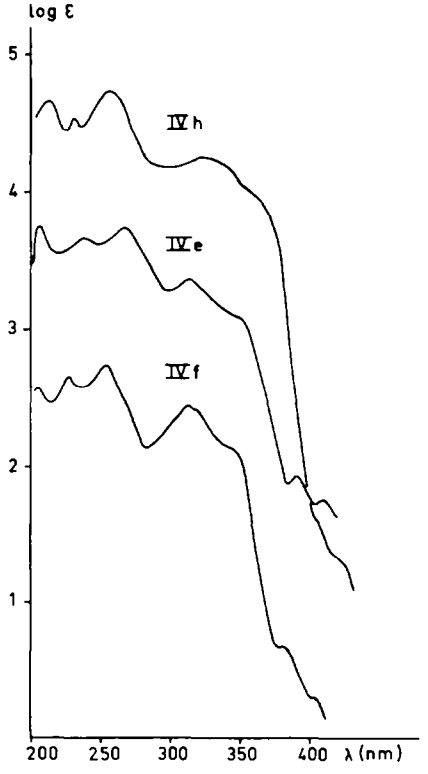


FIG 4. UV spectra of 2-*p*-tolylhexahelicene (IVe); 3-methylhexahelicene (IVf) and 1,3-di t-butylhexahelicene (IVh) in methanol. IVe and IVf are, with regard to IVh, shifted respectively 1 and 2 log units

An estimation of the distance between C_1-substituents and C_{25} depends on the orientation of the substituent-C_1 bond. Herraez assumed this direction parallel to the reference plane through C_{21}—C_{22} and calculated 2·70 Å for this distance. A similar assumption applied to Kitaigorodsky's model leads to a value of 2·17 Å.

Therefore, in the Herraez model substitution of a Me group with a radius of 2·0 Å according to Pauling[20] at position 1 should be possible without any new steric interference; with a t-Bu substituent the situation should become just critical. Only in Kitaigorodsky's model substitution of larger alkyl residues appears to be impossible without conformational changes. Our results are in better agreement with the latter model.

(3) *The UV spectra.* The UV spectrum of hexahelicene has been analysed by Weigang *et al.*,[3] who showed that the wavelengths of maximum absorption of the α,p and β bands were quite normal in comparison with the same bands of lower benzologues. No specific effect of non-coplanarity was visible.

In Table 4 the wavelengths and log ε-values of the maxima in the spectra of the hexahelicene derivatives are given. In Fig 4 three representative spectra are shown.

As can be seen from the Table all spectra are on the whole very similar. There are small variations in wavelength due to the alkyl substituent, but even 2-*p*-tolylhexahelicene (IVe) does not show large differences from the other ones; the slight broadening and the small bathochromic shift of all bands can be an indication of extended conjugation.

In the spectra of 1-substituted compounds an indication of small changes in steric relations can be seen in the bathochromic shift of the α- and p-bands and the loss of fine-structure. According to Murrell[13] the direction of the p-band shift caused by steric hindrance can be predicted from the change in energy of the highest occupied orbital of an aromatic compound. In the highest occupied molecular orbital (HOMO) of hexahelicene the bonds 1–2 and 1–17 have no nodal plane. By twisiting these bonds and so reducing the value of the resonance integral, the energy of the HOMO will increase, which in turn results in a bathochromic shift of the p-band. The p-band shift in IVh (10 nm), significantly larger than that caused by the alkyl substitution in the other compounds (1–3 nm) may point to the appearance of such deformations in the substituted ring of IVh.

The α-bands in IVa, g and h show a rather large bathochromic shift, in IV h accompanied with a dramatic decrease in extinction and loss of vibrational fine-structure in all bands. A similar difference has been found between the spectra of 4,5-dimethylphenanthrene and phenanthrene.[16] Analogous effects have also been observed in all prominent bands in the spectrum of benzo[*c*]phenanthrene on Me substitution[14] at position 1, quite different from the small shifts associated with substitution at any other position. Hirschfeld[15] gave a theoretical foundation for these findings.

In conclusion it can be said that the UV data confirm the results of the NMR analyses in that substitution at C_1 of hexahelicene with bulky groups causes real changes in the helix conformation.

EXPERIMENTAL

The UV spectra were recorded with a Beckman DK2A or a Cary 15 spectrophotometer. The mass spectra were obtained with a Varian MAT SM2B mass spectrometer. Starting compounds were prepared by known methods: Sommelet reactions in the syntheses of aldehydes, side chain brominations by N-bromosuccinimide (NBS) in CCl_4 in the preparation of bromomethyl derivatives. The bromides were used without purification in the preparation of triphenylphosphonium salts.

In general Wittig reactions were performed in ethanolic soln with $NaOCH_3$ as base. Only in the synthesis of IIIb DMF was used as solvent.

TABLE 4. UV SPECTRA OF SUBSTITUTED HEXAHELICENES. IN METHANOL λ_{max} IN NM; LOG ε IN PARENTHESIS; INFLECTIONS IN BRACKETS

No.	α	*p*	β	β′
	407 (2·47); 387 (2·79)	345 (4·09)	323 (4·43) ; 312 (4·45)	[300 (4·26)]; [287 (4·14)]; 260 (4·72) ; 253 (4·76); [247 (4·71)]; 228 (4·68)
IVa	417 (2·98); 396 (2·99)	[348 (4·08)]	[325 (4·36)]; 317 (4·38)	[305 (4·22)]; [293 (4·14)]; [263 (4·61)]; 255 (4·66); [250 (4·63)]; 231 (4·59)
IVb	410 (2·76); 388 (2·92)	347 (4·10)	324 (4·41) ; 313 (4·47)	[303 (4·28)]; [288 (4·18)]; [259 (4·78)]; 256 (4·80); [247 (4·75)]; 230 (4·75)
IVc	406 (2·65); 388 (2·83)	347 (4·09)	325 (4·39) ; 313 (4·45)	[301 (4·27)]; [288 (4·15)]; [262 (4·72)]; 255 (4·76); [248 (4·71)]; 231 (4·72)
IVd	408 (2·60); 388 (2·77)	346 (4·09)	324 (4·36) ; 313 (4·42)	[301 (4·25)]; [288 (4·18)]; [261 (4·70)]; 254 (4·74); [248 (4·71)]; 230 (4·71)
IVe	410 (2·75); 390 (2·92)	[348 (4·08)]	[330 (4·27)]; 316 (4·37)	[303 (4·27)]; 265 (4·74) ; 239 (4·66)
IVf	405 (2·30); 384 (2·68)	[344 (4·11)]	[316 (4·44)]; 312 (4·45)	[305 (4·28)]; [285 (4·17)]; [258 (4·54)]; 252 (4·75); 227 (4·27) ;
IVg	417 (2·54); 394 (2·76)	[349 (4·10)]	[325 (4·42)]; 318 (4·18)	[305 (4·02)]; [292 (3·88)]; [263 (4·67)]; 255 (4·75); [250 (4·74)]; 232 (4·64)
IVh	426 (1·30); 407 (1·60)	[355 (4·01)]	[330 (4·23)]; 320 (4·26)	[305 (4·22)]; [290 (4·21)]; 256 (4·75) 231 (4·56)

The irradiations were carried out in benzene solns with I_2 added as an oxidant. As a light source four Sylvania blacklite F8T5 lamps surrounding a pyrex tube of 750 ml were used.

Identity and purity of all compounds were checked by NMR, IR and mass spectra. M.ps were estimated on a m.p. microscope and are uncorrected.

Physical data of the hexahelicenes have been given in Tables 1–4

2-Methylbenzo[c]*phenanthrene* was synthesized by photodehydrocyclization of *p*-methylstyrylnaphthalene in 70% yield, m.p. 79–81°.

Bromination and reaction with triphenylphosphine gave the phosphonium bromide (I) in 80% yield and with m.p. 320–321°

1-Methyl- and 3-methylhexahelicene (IVa and IVf). A Wittig reaction of I and *m*-methylbenzaldehyde (bp: 60 62°/3 mm Hg) gave IIIa in 75% yield. *trans*: m.p. 150–150·5°; UV (methanol) λ_{max} in nm (log ε): 390 (2·71); 352 (4·22); 337 (4·33); 318 (4·47); 304 (4·57); 297 (4·57); 265 (4·58); 249 (4·49); 233 (4·49); 215 (4·63); 208 (4·69). On irradiation of IIIa a mixture of IVa and IVf was obtained. It was roughly separated by column chromatography on silica. A first fraction, eluted with hexane, contained mainly IVa with some IVf. A second fraction was rather pure IVf. Repeated chromatography of the latter on alox and crystallization from MeOH gave pure IVf with m.p. 186–188°. The first fraction was again chromatographed on a thick layer and a column of silica. Final crystallization from MeOH gave pure IVa with m.p. 175–176°.

2-Methylhexahelicene (IVb). A Wittig reaction of I and *p*-methylbenzaldehyde yielded IIIb in 50% yield, *trans*: m.p. 117–118°; UV λ_{max} in nm (log ε): 394 (2·96); 356 (4·41); 341 (4·50); 319 (4·58); 308 (4·62); 301 (4·60); 267 (4·58); 251 (4·44); 241 (4·42); 234 (4·43); 216 (4·49). Irradiation gave IVb.

2-i-Propylhexahelicene (IVc). Compound IIc was prepared according to Klouwen and Boelens,[17] b.p. 68°/1 mm Hg. The Wittig reaction with I and IIc yielded 90% of 1-(*p*-isopropylphenyl)-2-(2-benzo[c]phenanthryl)ethylene, *trans*: m.p. 107°; UV (MeOH) λ_{max} in nm (log ε): 392 (3·04); 356 (4·50); 330 (4·57); 307 (4·63); 299 (4·66); 256 (4·57); 239 (4·46); 229 (4·45); 222 (4·47).

The product was converted into IVc by irradiation.

2-t-Butylhexahelicene (IVd). Compound IId was also prepared as described by Klouwen and Boelens.[17]

A Wittig reaction of I and IId gave IIId in 89% yield, *trans*: m.p. 111–112°; UV (MeOH) λ_{max} in nm (log ε): 389 (2·99); 355 (4·43); 339 (4·50); 316 (4·57); 307 (4·61); 266 (4·54); 232 (4·44); 211 (4·50).

By photodehydrocyclization of IIId, IVd was obtained.

2-p-Tolylhexahelicene (IVe). Bis *p*-tolyl was synthesized from *p*-bromotoluene by the Kharasch method[18] (m.p. 117–121°). The product was monobrominated by NBS and the 4-bromomethyl-4′-methylbiphenyl converted into the corresponding aldehyde (IIe) by a Sommelet reaction in AcOH. The aldehyde was crystallized from EtOH–water and had m.p. 230–234°. IIe reached with I under formation of IIIe in 70% yield, *trans*: m.p. 183–187°; UV (MeOH) λ_{max} in nm (log ε): 395 (3·53); 380 (4·02); 362 (4·32); 350 (4·23); 307 (4·46); 265 (4·65); 259 (4·65); 238 (4·66); 213 (4·52).

On irradiation IIIe gave IVe.

1,3-Dimethylhexahelicene (IVg). Compound IIg was synthesized from mesitylene by singular bromination followed by a Sommelet reaction. b.p. 223–225°/760 mm. By the usual Wittig procedure with IIg and I IIIg was obtained in 80% yield, *trans*: m.p. 165–166°; UV (MeOH) λ_{max} in nm (log ε) 395 (2·79); 354 (4·13); 340 (4·26); 318 (4·42); 303 (4·53); 297 (4·53); 267 (4·57); 249 (4·47); 215 (4·60); 298 (4·62).

Irradiatiion of IIIg yielded IVg.

1,3-Di-t-butylhexahelicene (IVh). Benzo[c]phenanthryl-2-aldehyde was prepared by a Sommelet reaction of the corresponding bromide in 50% yield, m.p. 94·5–96°.

3,5-Di-t-butyltoluene m.p. 31–32° was synthesized according to Geuze.[19] Subsequent reactions with NBS and triphenylphosphine gave the triphenylphosphonium salt of 3,5-di-t-butylbenzylbromide in 80% yield with m.p. 322–324°. This salt and benzo[*c*]phenanthryl-2-aldehyde could be converted into IIIg in 90% yield, *trans*: m.p. 56–60°; UV (MeOH) λ_{max} in nm (log ε): 393 (2·40); 372 (3·68); 356 (4·29); 341 (4·39); 318 (4·50); 307 (4·56); 302 (4·54); 267 (4·54); 250 (4·44); 233 (4·43); 215 (4·56).

From an irradiation mixture of IIIg, IVg could be isolated though in very low yield.

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