Tetrahedron. Vol. 28, pp. 1803 to 1810. Pergamon Press 1972. Printed in Great Britain

CONFORMATIONAL STUDIES ON HEXAHELICENES—I

THE NMR SPECTRA OF THE BENZOHEXAHELICENES

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(*Received in the UK* 16 *November* 1971; *Accepted for publication* 2 *December* 1971)

Abstract—The NMR spectra of the benzohexahelicenes have been analyzed. The conformation of the helical structure is not changed to a large extent by the benzo-groups. Some flattening of a part of the helix results in a small downfield shift of the protons on the terminal rings and in a larger upfield shift of proton A in II ascribed to a change in the ring current in the pitch of the helix. A gradual upfield shift is found for protons of the terminal rings by an increase in overcrowding of the benzo-groups.

INTRODUCTION

IN A previous paper[1] we concluded from the polarographic reduction potentials of eight helicenes, including the benzohexahelicenes II–V, that all these molecules deviate from coplanarity to a similar extent. As a property of the molecule as a whole, the polarographic reduction potential, however, does not reveal small local differences in conformation between the individual benzohexahelicenes. To investigate such details we analyzed the NMR spectra, which seem to be more apt to give a more detailed picture of helicene conformations as was shown by Martin *et al.*[2] in a comprehensive NMR analysis of nonahelicene and its lower benzologues.

First, it was of interest to know what kind of influence the additional benzo group in compounds II–VI would have on the protons of the overcrowded terminal rings. With reference to earlier investigations it was expected that going from I to VI a gradual increase in shielding of these protons would be observed.

Furthermore, because the helicenes are not planar, the attachment of a benzo group will have another, probably a smaller, steric effect on the new angular α_3-protons* than is the case in planar molecules like phenanthrene and triphenylene.

Finally, the NMR spectra should give a definite proof of structure of the compounds synthesized.[3]

RESULTS AND DISCUSSION†

In contrast to hexahelicene (I) which contains a double set of eight different protons (A–G, Fig 1), the benzohexahelicenes (II–V) do not possess any symmetry and all protons are in principle anisochronous.

In nearly all cases all protons could be located in the spectra by decoupling and tickling experiments.

Because of the low solubility of compound V in $CDCl_3$ and CCl_4 all compounds were measured in CS_2 solution containing 5% TMS as an internal reference.

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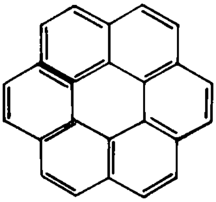
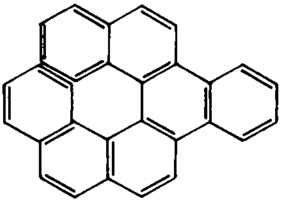
* Nomenclature in accordance with Martin, *Tetrahedron* **20**, 897 (1964)

† Spectra were measured with a Varian HA100 spectrometer.



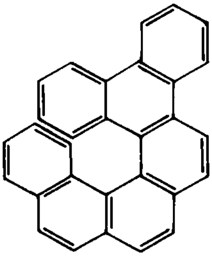
I

hexahelicene



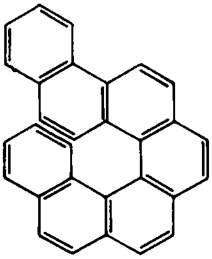
II

benzo[d]
hexahelicene



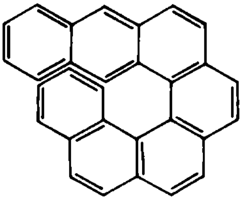
III

benzo[*a*]
hexahelicene



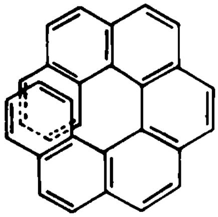
IV

benzo[*m*]
hexahelicene



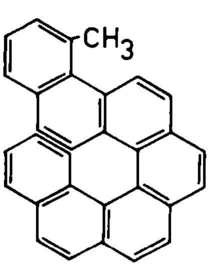
V

benzo[*n*]
hexahelicene



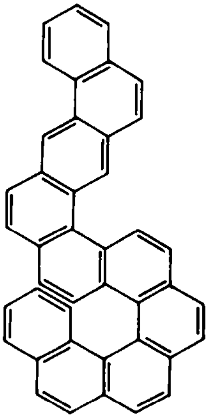
VI

heptahelicene



VII

methyl benzo[*m*]
hexahelicene



VIII

benzo[*a*]
hexaheliceno[*h*]
anthracene

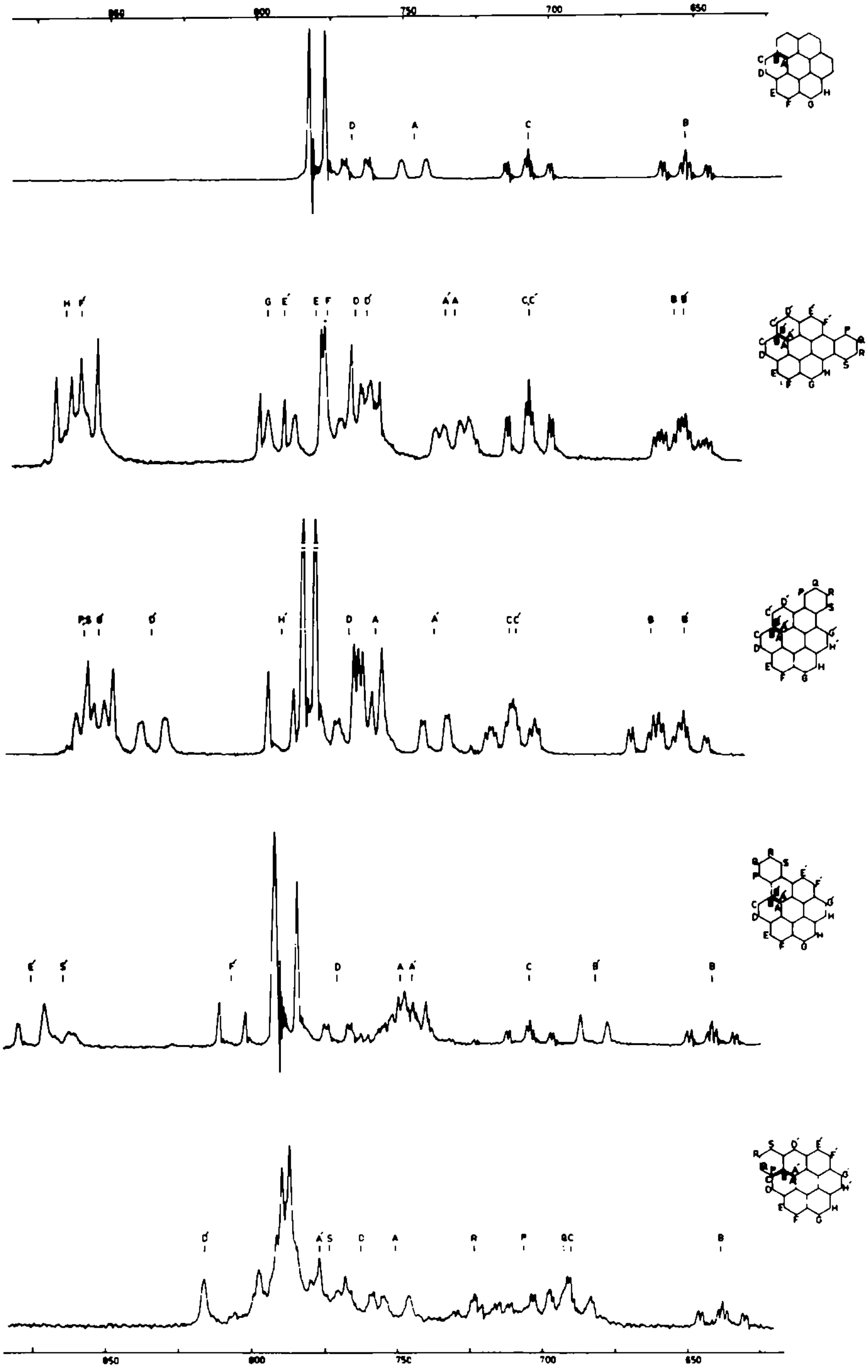


Fig 1. The NMR spectra of hexahelicene and the benzohexahelicenes in CS_2 solution (100 Mc/s)

However, differences in chemical shift for different solvents are small and rather constant for most protons in this type of compounds, as can be seen in Table 1 for compounds I, III and VI.

TABLE 1

δ CDCl$_3$ $-\delta$ CS$_2$ in c/s for compounds III, I and VI

III				I*		VI*			
A	12	A′	12	A	12	A	14	G	5
B	11	B′	10	B	12	B	11	H	9
C	10	C′	11	C	10	C	11	I	7
D	11	D′	13	D	11	D	13		
E	12			E, F	10	E	12		
G	10	G′	9	G, H	9	F	8		

* The frequencies of I and VI in CDCl$_3$ solution are taken from Martin.[2]

Frequencies were estimated by the side band technique. The frequencies of different protons showed a varying dependence on concentration, as is illustrated for compound III in Table 2. The effect is not very large, but clearly more pronounced for unhindered protons (G, H′).

TABLE 2. δ-VALUES OF PROTONS IN BENZO[*a*]HEXAHELICENE (III) AT DIFFERENT CONCENTRATIONS IN CS$_2$ AND CDCl$_3$

	12% w/v	δ in ppm (CS$_2$) Infinite dil.	Δ in c/s	12% w/v	δ in ppm (CDCl$_3$) Infinite dil.	Δ in c/s
A	7·54	7·55	1	7·65	7·67	2
B	6·56	6·61	5	6·66	6·72	6
C	7·06	7·14	8	7·16	7·24	8
D	7·61	7·69	8	7·71	7·80	9
E	7·73	7·80	7	7·81	7·92	11
G	7·77	7·89	12	7·85	7·99	14
A′	7·28	7·31	4	7·40	7·43	3
B′	6·45	6·52	7	6·56	6·62	6
C′	7·04	7·10	6	7·16	7·21	5
D′	8·28	8·33	5	8·40	8·46	6
H′	7·86	8·01	15	7·93	8·10	17

The concentration dependence of the chemical shifts of protons A–H′ is as expected because in concentrated solutions mutual ring current influences between the aromatic molecules are less in overcrowded regions.[4] Thus protons in the central part of the molecule are more sensitive for larger separations (dilution). The concentration effect is negligible in the compounds I and VI as already stated by Martin, in the case of solutions in benzene[2] and CS$_2$.*

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* Personal communication of Prof. Martin

For a relevant discussion of the NMR data each compound was measured at several concentrations and the frequency at infinite dilution estimated by extrapolation was used. Because not all compounds could be measured in the same concentration range, the results of extrapolation for compounds with a low solubility are not as accurate as for other ones. The accuracy of the frequencies is estimated at ±0·3 c/s for well resolved maxima. In cases where proton signals overlap or the signal-to-noise ratio was not very good, the error may be about 1 to 3 c/s, so that we estimate the accuracy within the whole series to be ±2 c/s though the accuracy within the spectrum of each individual compound for most protons is 0·3.

Spin-spin coupling constants were also estimated from the spectra. Within the error of estimation, all coupling constants appeared to be equal for equivalent protons in the whole series.

To justify the assignment of the chemical shifts of the different protons and the coupling constants the spectra were simulated with the aid of the LAOCN-3 program on an IBM 360-50 computer. In Table 3 the chemical shifts (δ) in ppm and the spin–spin couplings constants (J) are tabulated.

To facilitate the discussion the protons have been subdivided in three groups: (1) protons in the overcrowded region (A–G); (2) protons at angular α_3-positions; (3) other protons.

(1) In Fig 2 the frequencies of the protons of the first group are graphically represented. To explain the changes of the chemical shifts using hexahelicene as a standard, it is assumed that they are mainly due to varying ring current effects. Though in general σ-bond anisotropies can also be of influence[5] these effects appear

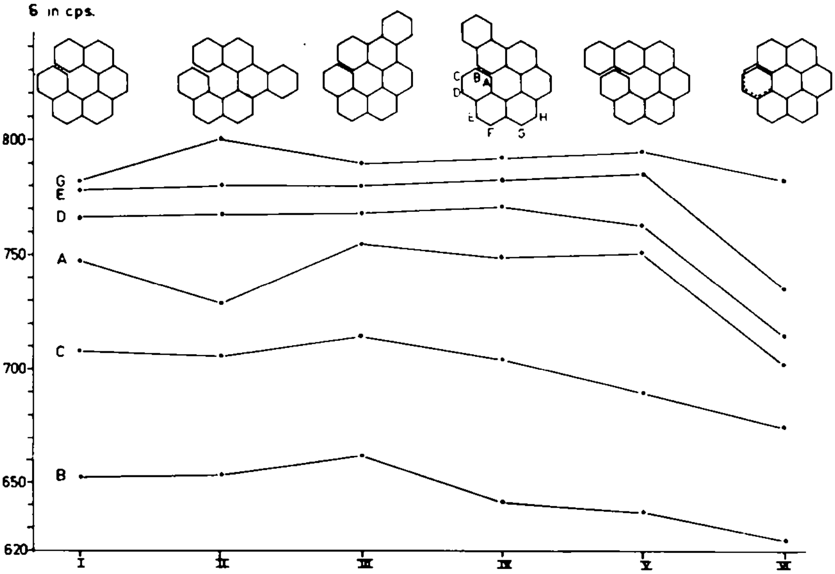

FIG 2. Influence of a benzo-group attached to hexahelicene at different positions on the chemical shift of the A, B, C, D, E and G protons (100 Mc/s)

to be small even in a series of quite different aromatics,[6] and will be negligible in a series of closely related compounds.

Three kinds of effect then deserve attention in the interpretation of upfield or downfield shifts.

1. The proton under investigation is in closer proximity to the opposite ring as a result of torsion in the helix.
2. The proton is influenced by the ring current of the new ring (benzo group).
3. The proton is influenced by an increase in the ring current of some relevant aromatic nucleus.

Fig 2 seems to indicate that going along the series I–VI there is a slight general increase in δ-values for several protons. This trend is especially clear for protons D, E and G (only compound VI is an exception). These small effects may be ascribed to the additional ring in compounds II–VI. Its ring current influence will be small, because all relevant protons (except G in II) are rather far removed from the additional benzo group. This is in accordance with Bernstein, *et al.*[4] who observed that the influence of an aromatic nucleus added to a polycyclic aromatic on some proton elsewhere in the molecule decreases with the third power of the distance. The increase of this effect going from II–V (compounds with the same number of nuclei) may be explained by the fact that the influence mentioned is also dependent on the angle (θ) between the relevant proton and the benzo group, which varies as the position of the benzo group on the helix is changed (factor $1-3\cos^2\theta$).[7]

Similar small variations in δ expected for protons A, B and C remain apparently hidden by larger effects from other causes.

Some more pronounced downfield shifts (A, B, C in III) may be due to a flattening of the phenanthrenic part (A'B'C'D'PQRS) or better the triphenylenic part (A'B'C'D'PQRSG'H') of the molecule as a consequence of the addition of a benzo group. This should result in a stronger torsion in the remaining part of the helix and a rather large difference in the frequencies of protons A and A' (24 c/s; A' is even shifted to higher field in comparison with I). The chemical shift difference between protons B and B' in III is by this effect should be smaller, as is found (9 c/s).

As Martin[2] showed for the series of benzologues of hexahelicene, extension of the overlapping regions at the ends of the helical chain causes a gradual shift to higher field for protons in these areas. Similar rather large upfield shifts are also found for compounds IV (B and C), V (B, C and D) and VI (A, B, C, D, and even E, F).

The A proton in II deserves special attention. The remarkable low δ-value cannot be made comprehensible by one of the effects mentioned. This is because the distance to the benzo group added is large and variations in torsion at the ends of the molecule would result in a higher δ-value of A' or larger differences in the positions of B and B', and possibly C and C'.

Knauer[8] suggested that the position of the A proton signal in the NMR spectrum is strongly dependent on the intensity of a ring current in the pitch of the helix, which must be present if a bond integral (β) different from zero is accepted between the C atoms A and A'. Knauer calculated that a change in β of 0·01 units shifts the A proton more than 17 c/s, whereas the positions of other protons are rather insensitive to variations in β. This is exactly what is observed in II. Such a little increase in β can be caused by the benzo group, which will make the triphenylenic part of II slightly more planar resulting in a shorter distance between A and A'. Though Knauer concludes from his experiments that there is little electronic interaction between A and A′ (see however the following paper) the assumption of a ring current to explain the high field signal for proton A (in II) seems still worthwhile and deserves renewed theoretical study.

(2) *Protons at an angular phenanthrenelike* (α_3) *position.* These protons and their chemical shifts are II F′ (8·60); II H (8·68); II P (8·68); II S (8·68); III D′ (8·33); III G′ (8·59); III P (8·56); III S (8·56); IV S (8·61); IV E′ (8·74). For a comparison, the frequencies of the protons 4 and 5 of phenanthrene and triphenylene in CS_2 were found to be 8·51 and 8·50 resp. and the α_3-proton in compound VIII 8·75. In the latter compound no special overcrowding effect is expected for the phenanthrenelike part of the molecule. Haigh[10] found for this kind of protons in 11 compounds a range from 848–898 c/s (perylene 811).

In our series III D′ is the only one outside this range. It is also the only proton in the series influenced by the ring current of the opposite ring, which explains the high δ-value.

TABLE 3. CHEMICAL SHIFTS IN δ OF THE ARYLOHEXAHELICENES IN CS_2 SOLUTION

	I	II	III	IV	V	VI	VII	VIII
A	7·47	7·29	7·55	7·49	7·51	7·01	7·53	
B	6·53	6·54	6·61	6·42	6·38	6·27	6·37	6·44
C	7·08	7·06	7·15	7·04	6·91	6·76	6·97	6·97
D	7·67	7·68	7·69	7·71	7·63	7·15	7·63	
E	7·77	7·80	7·80	7·84	7·85	7·35	7·79	
F		7·78				7·61		
G	7·82	8·00	7·89	7·92	7·95	7·83	7·89	
H		8·68				7·85		
A′		7·32	7·31	7·43	7·77		7·38	7·46
B′		6·52	6·52	6·85	—		6·79	6·95
C′		7·06	7·10	—	—		—	
D′		7·64	8·33	...	8·17		·	
E′		7·94	—	8·74	7·85		8·78	
F′		8·60	—	8·07			7·90	
G′		—	8·59	7·93				
H′		—	8·00		7·95			
P		8·68	8·56	7·50	7·06		7·31	
Q		~7·60	7·69		6·90			
R			7·61	7·40	7·22			
S		~8·68	8·56	8·61	7·75			

Spin–spin couplings constants (*J*) in the arylohexahelicenes

JAB = 8·5   JA′B′ = 8·5
JAC = 1·3   JA′C′ = 1·3
JAD = 0·5   JA′D′ = 0·5
JBC = 6·8   JB′C′ = 6·8
JBD = 1·4   JB′D′ = 1·4
JCD = 7·9   JC′D′ = 7·9
JEF = 8·5   JE′F′ = 8·5
JGH = 8·5   JG′H′ = 8·5

epicouplings were found in
II   JA′E′ = 0·3
IV   JA′E′ = 0·3
      JB′S = 0·3

The chemical shift difference of the protons E′ in VII and E′ in IV (4 c/s) is surprisingly small when compared with the difference in frequency between H_5 in phenanthrene and H_5 in 4-methylphenanthrene (23 c/s).[9] This might be due to the nonplanarity of the relevant phenanthrenic part in IV; substitution of proton S by CH_3 does not increase the interaction with E′ very substantially.

(3) *Other protons.* Going along the series II–V, the P, Q, R and S protons show a regular high field shift if they are not in α_3-positions. This shift is to be expected by the increasing influence of overcrowding. The protons A′ and D′ of V are anthracenic γ-protons. Both, but especially A′ show a large upfield shift in comparison with the normal frequency at about 8·30 (compare in VIII: $\gamma_3 = 9{\cdot}07$, $\gamma_4 = 9{\cdot}56$).

Acknowledgement —We wish to thank Mr. H. F. Smeets and Mr. J. M. F. Mous for their skillful assistance in the measuring of the NMR spectra, and Prof. R. H. Martin (Free University of Bruxelles) and Dr. C. W. Haigh (University College Swansea) for their interest and correspondence.

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