Tetrahedron. Vol. 25, pp. 4985 to 4998. Pergamon Press 1969. Printed in Great Britain

STUDIES IN NMR SPECTROSCOPY[1a]

THE HELICENES AND LOWER BENZOLOGUES[1b, 1c]

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(*Received in the UK* 9 *June* 1969; *Accepted for publication* 2 *July* 1969)

Abstract—This paper reports the results of a comparative study of the NMR spectra of phenanthrene to nonahelicene (I–VII, Fig. 1). The four spin systems present in these hydrocarbons (end rings) have been calculated and the corresponding protons (A, B, C, D) have been assigned on the basis of the coupling constants. These assignments are fully confirmed by the study of substituted derivatives, *epi* cross-ring couplings and specific solvent effects. The repercussion of the progressive overlap of benzene rings on the NMR spectra is discussed.

Résumé—Ce travail est consacré à l'étude comparative des spectres de RMN des composés I à VII (Fig. 1). Les systèmes à quatre spins présents dans ces hydrocarbures (cycles terminaux) ont été calculés et les protons correspondants (A, B, C, D) ont été attribués sur la base des constantes de couplage. Ces attributions sont confirmées par l'étude de dérivés substitués, de couplages intercycles *épi* et d'effets de solvant spécifiques. Une brève discussion concernant l'influence du recouvrement progressif des noyaux benzéniques sur les spectres de RMN, complète cette étude.

INTRODUCTION

THE benzologue hydrocarbons phenanthrene (I), benzo[*c*]phenanthrene (II), dibenzo-[*c*, *g*]phenanthrene (III), hexahelicene§ (phenanthro[3.4-*c*]phenanthrene) (IV), heptahelicene (benzo[*c*]phenanthro[4.3-*g*]phenanthrene) (V), octahelicene (naphtho [2.1-*c*] phenanthro[4.3-*g*]phenanthrene) (VI) and nonahelicene (*bis*phenanthro [3.4-*c*; 4′.3′-*g*]phenanthrene) (VII), are a particularly interesting series of polycondensed aromatic hydrocarbons. The progressive angular annelation produces increasing deviation from coplanarity[2-4] to reach complete overlap of respectively two, four and six aromatic rings in hepta-, octa- and nonahelicene. In the present work, we have examined the repercussion of these geometrical distortions on the NMR-spectra of the above mentioned hydrocarbons.

GENERAL DESCRIPTION OF THE SPECTRA AND ASSIGNMENT OF THE DIFFERENT PROTONS

A helicene or lower benzologue with n rings contains $n + 2$ different kinds of protons and two protons of each kind, the molecule being symetrical from the NMR point of view. The spectra of these hydrocarbons thus consists of:

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† Chargé de Recherches du "Fonds National Belge de la Recherche Scientifique".

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§ We suggest that individual members of the helicene series be designed either by a numerical prefix or by a number enclosed in square brackets placed immediately before the generic name helicene: e.g. octahelicene or [8]helicene.

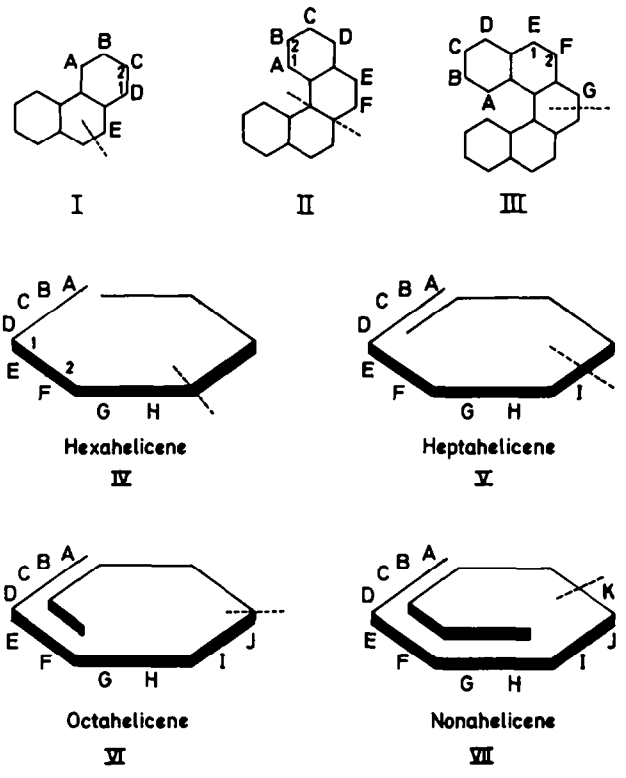


FIG. 1.*

(a) Two identical four spin systems (the 8 protons of the end rings) and

(b) Either $(n-2)/2$ pair of identical two spin systems ($n-2$ doublets containing 2 H each) when n is even, or $(n-3)/2$ pair of identical two spin systems ($n-3$ doublets containing 2 H each) and one singlet containing 2 protons (central ring) when n is *odd*.

This general description is but a first approximation as it does not take into account the small cross-ring couplings[5] present in fused benzenoid hydrocarbons (vide-infra). The NMR spectra of the seven hydrocarbons considered in this work have all been published, some of them without comments: I,[6-8] II,[9-10] III,[10] IV[11] (40 Mc/s), V,[12] VI and VII.[13] The spectrum of phenanthrene (I) is the only one† which has already been treated mathematically[8] and in which each type of proton has been assigned unambiguously. In order to carry out a comparative study, we have recorded the spectra of I–VII at 60 Mc/s in $CDCl_3$ and C_6D_6 solutions (10% w/v or saturated solutions) on a Varian A60 spectrograph (sweep width: 1 c/s = 5 mm; TMS = 0).

For the mathematical analysis of the four (A, B, C, D) and six (A, B, C, D, E, F) spin systems present in these molecules we have adapted the LAOCOON program described by Castellano and Bothner-By[14] to the IBM 7040 computer of the "Centre de Calcul Numérique et Analogique de l'Université Libre de Bruxelles". Confrontation

* I to VII represent fully aromatic hydrocarbons.

I, II, III and IV: present IUPAC numbering. The numbering of the helicenes should be seriously reconsidered (cf. Newman, ref. 11, footnote 1).

† See Addenda.

between experimental and calculated spectra is facilitated by the use of a NMR PLOT program* drawing the calculated spectra and assuming a lorentzien profile[15] for each calculated transition. Agreement between the calculated and observed spectra is realized in an iterative way and the process is stopped when an agreement of $\pm 0{\cdot}1 - \pm 0{\cdot}2$ c/s is obtained for each maximum. The estimated error on the calculated chemical shifts of individual protons does not exceed 0·2 c/s; in the case of octa- and nonahelicene however, the error may be as large as 0·6 c/s (lower resolution of the experiment spectra). The results are collected in Table 1 and the experimental spectra ($CDCl_3$ soln) are shown diagrammatically on Fig. 2.

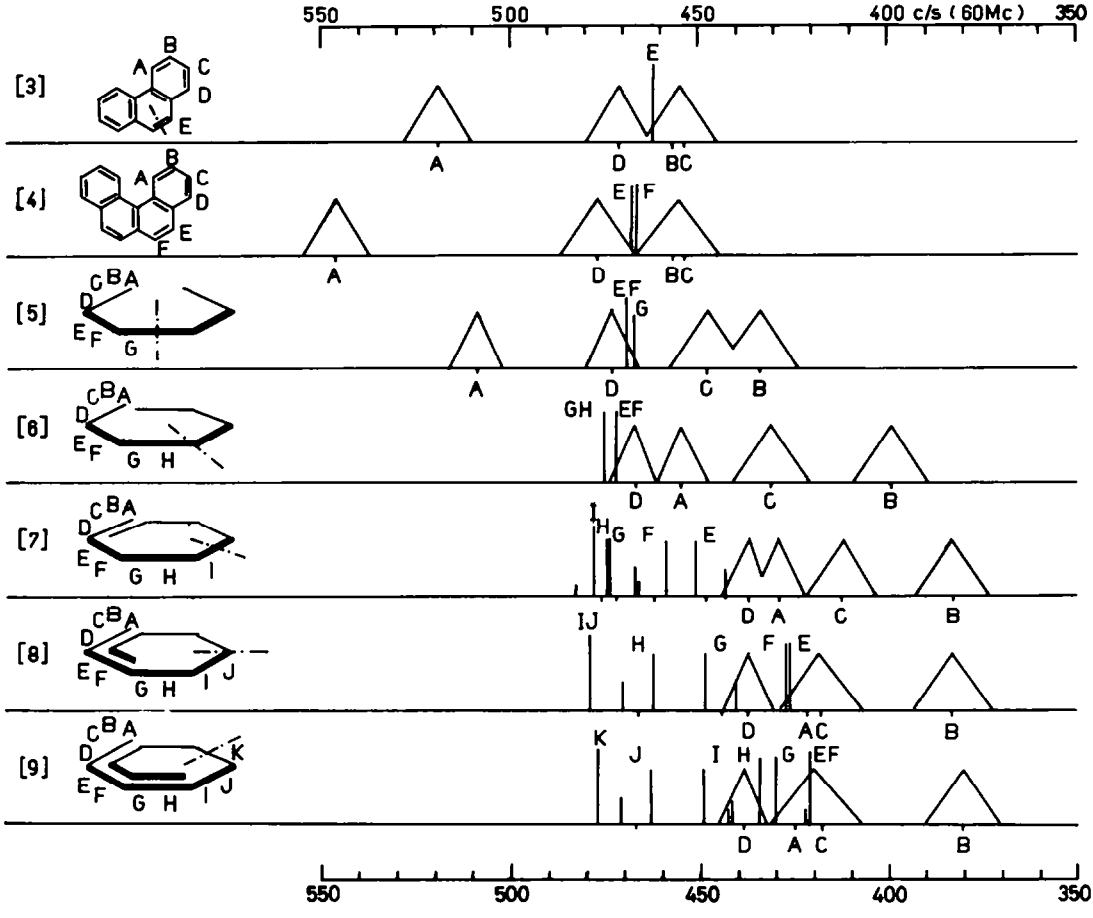


FIG. 2. Diagrammatic representation of the NMR spectra of the helicenes and lower benzologues. Solvent: $CDCl_3$ (60 Mc/s).

* Fortran listings of the NMR PLOT computer program can be obtained from the authors.

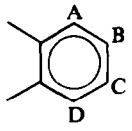
TABLE 1. NMR SPECTRA OF HELICENES AND LOWER BENZOLOGUES
($CDCl_3$ and C_6D_6 solutions. Conc.: max. 10% w/v) Calculated chemical shifts and spin-spin coupling constants (c/s at 60 Mc).

	[3]	[4]	[5]	[6]	[7]	[8][c]	[9][c]
($CDCl_3$)	*b*						
A	518·88	545·9	508·8	455·0	429·3	421·3	424·6
B	456·72	457·2	433·9	398·8	382·6	383·0	380·2
C	454·20	453·7	448·3	430·7	412·5	417·7	417·5
D	471·30	477·2	473·5	466·7	436·7	437·5	438·6
E	462·12	469·1	469·5[a]	472·1[a]	448·1	424·3	421·6[a]
F	——	464·7			461·7	428·8	
G		——	467·6	474·9[a]	472·2	444·8	427·9
H			——		476·2	467·3	435·3
I				——	477·7	479·3[a]	445·0
J					——		467·0
K						——	476·6
(C_6D_6)							
A	506·6	545·0	515·2	469·8	444·1		
B	443·6	442·6	420·3	391·3	382·2		
C	441·6	441·6	436·1	419·9	406·6		
D	459·0	465·7	463·1	457·7	431·8		
E	449·4	456·9	459·9	461·5[a]	441·8	420·5	420[a]
F	——	452·2	456·4		453·8	424·5	
G		——	454·8	463·0[a]	462·2	436·7	
H			——		464·8	456·7	
I				——	466·3	466·6[a]	
J					——		459
K						——	466
J Values	*b*						
J_{AB}	8·4	8·4	8·5	8·5	8·5	8·5	8·5
J_{BC}	7·2	7·2	6·8	6·8	6·8	6·8	6·8
J_{CD}	8·11	8·11	7·9	7·9	7·9	7·9	7·9
J_{AC}	1·24	1·24	1·3	1·3	1·3	1·3	1·3
J_{BD}	1·31	1·31	1·4	1·4	1·4	1·4	1·4
J_{AD}	0·66	0·66	0·5	0·5	0·5	0·5	0·5
J_{AE}		0·5	0·5		0·8		
J_{EF}	——	8·5	8·6		8·6	8·6	
J_{GH}		——	——		8·4	8·3	8·4
J_{IJ}				——	——		8·3

[a] Non resolved signals, center of the "singlet"
[b] Determined by Fahey and Graham[8]
[c] Saturated solution, low concentration;
The accurate measurement of some protons in C_6D_6 solution has been hampered, so far, for technical reasons.

(a) *The four spin systems (end rings).* The four adjacent protons of the terminal rings give rise to four spin systems in which two protons (A and D) are of the

"α-naphthalene" type (J_o, J_m, J_p), while the other two (B and C) are of the "β-naphthalene" type (J_o, J'_o, J_m). Concerning the assignment of the protons, we have proved that, in each case, a permutation between A and D or B and C give rise to calculated spectra which are incompatible with the observed spectra (two examples are given in Figs 3 and 4). The assignment of protons A, B, C and D thus follows from the unambiguous assignment of one of them. In the case of phenanthrene (I), Fahey and Graham[8] have shown that the low-field proton H_4 (H-α3* −519 c/s), called A (Fig. 1), has the largest J_o and the smallest J_m of the two "α-naphthalene" type protons:



$$J_{AB} > J_{CD} \qquad [J_{AC} < J_{BD}] \tag{1}$$

We have now reached the conclusion that proton A, defined according to the above spin-coupling relations (1), is *always* the first proton of the helix (H-α4, H-α5, H-α6...) in the helicene series. This conclusion is fully supported by the study of substituted derivatives, *epi* cross-ring couplings and specific solvent effects.

[8] HELICENE

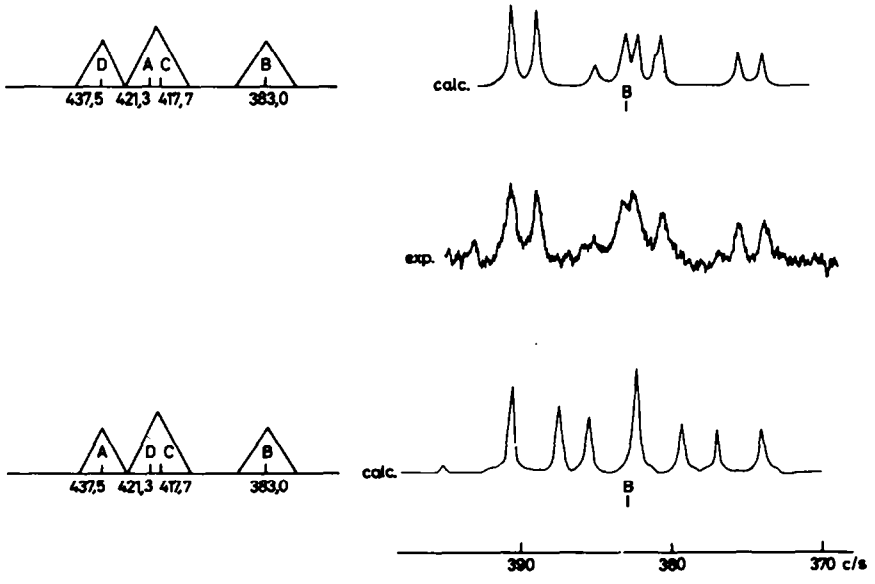


FIG. 3. Calculated spectra of the four spin systems (protons ABCD) of octahelicene obtained by the permutation of the chemical shifts of protons A and D. Pattern of the B protons (60 Mc/sec).

* For the meaning of these symbols, see ref. 1*b*.

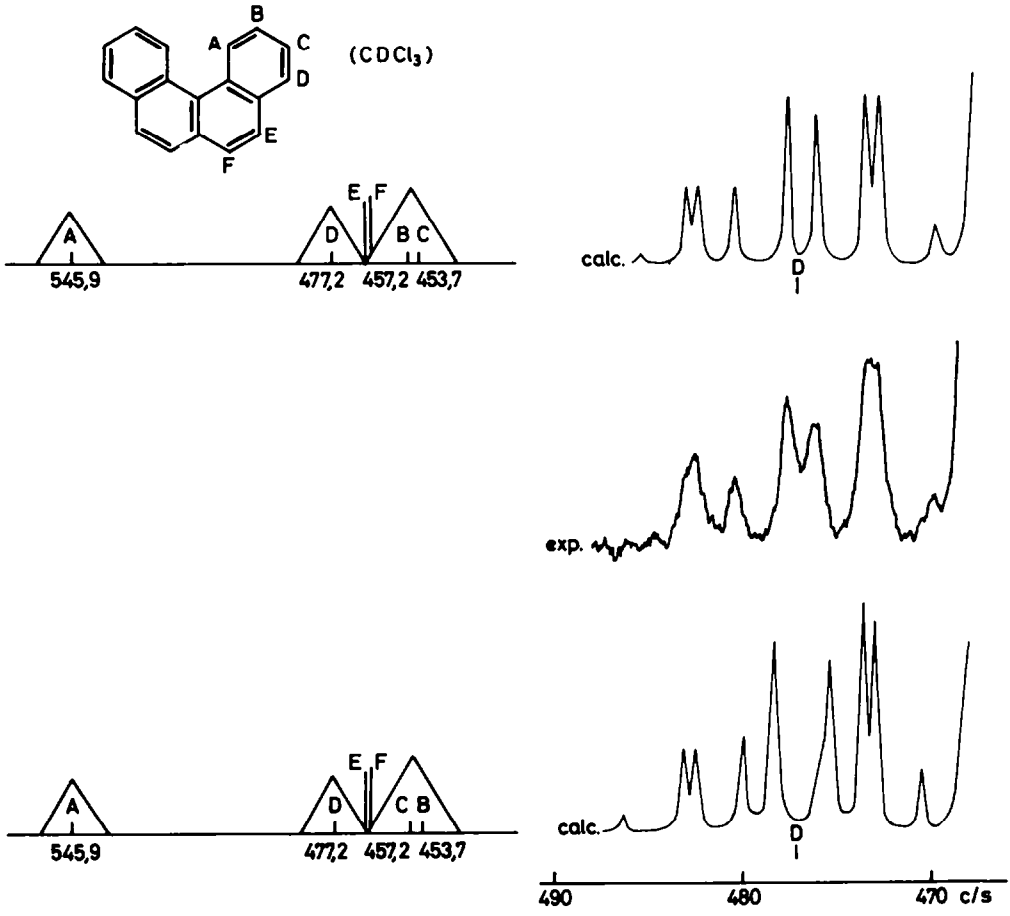


FIG. 4. Calculated spectra of the six spin systems (protons ABCDEF) of benzo[c]phenanthrene obtained by the permutation of the chemical shifts of protons B and C. Pattern of the D protons (60 Mc/sec).

1. *Substituted derivatives*

The NMR spectra of phenanthrene and benzo[*c*]phenanthrene derivatives, substituted in one of the end-rings, have been discussed in earlier publications from this and other laboratories.[7, 8, 16, 18] The synthesis of 11-methylphenanthro[3.4-*c*]-phenanthrene (2-methylhexahelicene according to Newman's nomenclature and numbering) has just been achieved by one of us (J.P.C.).[19] In the NMR spectrum of this derivative, the signal centered at 398 c/s and attributed to the B proton (391·3 c/s in hexahelicene) contains only one proton, as expected.

2. *Epi cross-ring couplings*

A comparison of the calculated ABCD systems of I–V with the observed spectra clearly shows that the signals of the B, C and D protons are better resolved than the signals of the A protons. This loss of resolution was first observed in phenanthrene

by Fahey and Graham,[8] who suggested that it could be due either to cross-ring couplings or to short relaxation time. Couplings of 0·3–0·4 c/s have also been measured between the sterically hindered H_4 and H_5 protons in 9- and 9,10-substituted phenanthrenes.[18d]

In the spectra of benzo[*c*]phenanthrene (II), dibenzo[*c*, *g*]phenanthrene (III) and heptahelicene (V), it is also quite clear that one doublet is not as sharp as the others. In view of earlier observations in this laboratory[5] of *epi* cross-ring couplings involving the protons A and E in substituted phenanthrene and benzo[*c*]phenanthrene derivatives ($J_{4.10}$ and $J_{1.5}$ respectively), it is highly reasonable to assume that similar *epi* cross-ring couplings exist in the unsubstituted hydrocarbons. The correctness of this view has now been confirmed in the case of benzo[*c*]phenanthrene (C_6D_6 solutions) by spin decoupling experiments carried out at 90 Mc/s.*

The calculated spectra of the ABCDEF six spin systems of II, III and V, including J_{epi}, are in good agreement with the observed spectra (see Fig. 5). It follows from the above considerations that protons A and E, and by way of consequence, protons B, C, D and F, can be unambiguously assigned in the NMR spectra of these molecules. chrysene.

3. *Specific solvent effects*

In a previous publication,[1c] we have reported the occurence of specific solvent effects ($CDCl_3$-C_6D_6) on the overcrowded protons (H-α4 and H-α5) of benzo[*c*] phenanthrene, dibenzo[*c*, *g*]phenanthrene, benzo[*g*]chrysene and dibenzo[*g*, *p*] crysene.

We have now extended this study to the helicenes series.

Specific solvent effects are not observed in the case of phenanthrene, the spectrum recorded in C_6D_6 being shifted, without any appreciable modification, to higher fields by 12–13 c/s. However, in the higher members of the series, the "non-hindered" protons are normally shielded, but the "hindered" protons are either hardly affected

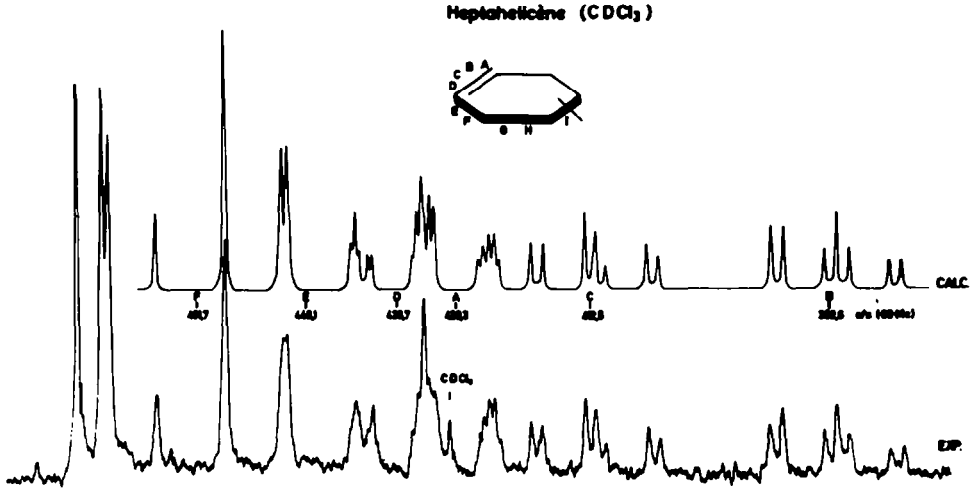


FIG. 5. Heptahelicene: experimental and calculated (6 spin ABCDEF) NMR spectra ($CDCl_3$ – 60 Mc/s).

* See also addenda.

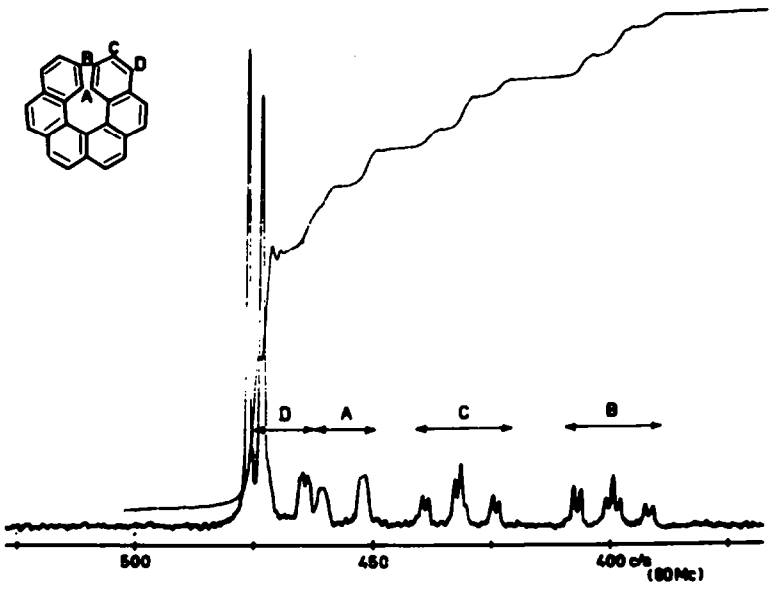


FIG. 6. NMR spectrum of hexahelicene in $CDCl_3$ (60 Mc/s).

TABLE 2. HELICENES: SOLVENT EFFECT
$\delta_{CDCl_3} - \delta_{C_6D_6}$ in c/s at 60 Mc.

Ring	Proton	[3]	[4]	[5]	[6]	[7]	[8]
1st	A	12	1	−6	−15	−15	
	B	13	15	14	8	0	
	C	13	12	12	11	6	
	D	12	12	10	9	5	
2nd	E	13	12	11	11	6	4
	F		13	11	11	8	4
3rd	G			12	12	10	8
	H				12	11	11
4th	I					11	13
	J						13

(+ 1 c/s for H_1 and H_{12} in II) or even deshielded (III–V). The results are collected in Table 2. The A protons show specific solvent effects which reflect the geometrical modifications introduced by the progressive angular annelation of benzene rings.

Similar but smaller effects are also observed on protons B, C and D in heptahelicene.

To complete this study, we have examined the influence of the concentration on the spectra of phenanthrene, benzo[*c*]phenanthrene and hexahelicene recorded in C_6D_6. In all cases, progressive dilution from 10% to 2·5% w/v solutions showed no appreciable specific effects: the protons are all shifted to slightly lower field (~ 1 c/s)

but the differences in chemical shifts between various protons remains constant within 0·8 c/s.

(b) *The two spin systems.* In the four hydrocarbons containing an odd number of rings, the two protons singlet of the central ring (E in I, G in III, I in V and K in VII) is easily identified.

In II, III and V, *epi* cross-ring couplings (J_{AE}) can be used to locate the signals of proton E, and by way of consequence, of proton F. In hexahelicene, the signals at 472·1 and 474·9 c/s ($CDCl_3$) [461·5 and 463 c/s in C_6D_6] correspond to EF and GH respectively. This attribution follows from the study of the NMR spectrum of phenanthro[3,4-*c*]phenanthrene-3-d_1(hexahelicene-7-d_1 according to Newman's nomenclature), recently synthesized by one of us (J.J.S).[36]

The other protons of the two spin systems of hepta-, octa- and nonahelicene are assigned on the basis of their chemical shifts (*vide infra*).

DISCUSSION OF THE RESULTS

(a) *Influence of the progressive overlap of benzene rings on proton chemical shifts*

1—*Four spin systems.* The repercussion of the progressive overlap of benzene rings on the chemical shifts of the A, B, C and D protons of the four spin systems is illustrated in Fig. 7. In the lower benzologues I and II (phenanthrene and benzo[*c*]phenanthrene), proton A is strongly deshielded relative to its theoretical position calculated by taking into account the combined effects of the ring-currents of the different rings* (δH_A calculated = 486·2 c/s in phenanthrene[20]). This discrepancy has been attributed to mutual Van der Waals compression effects between the overcrowded hydrogens.[20-22]

With increasing deviations from coplanarity of the aromatic systems in III to V, proton A is however progressively shifted to higher fields and a similar evolution is observed for protons B and C.

On the other hand, the chemical shift of proton D remains fairly constant in I–IV and an important shielding effect occurs only when complete overlap of the terminal rings of the helicene is reached (heptahelicene). It is also interesting to note that further annelation to octa- and nonahelicene no longer affects the resonance frequencies of the protons A, B, C and D of these terminal rings.

This is qualitatively the expected evolution for these protons on the basis of Waugh and Fessenden's[23, 24] distribution function of the effect of the induced diamagnetic ring-current of benzene rings in space. Similar up-field shifts have indeed been observed in other systems containing overlapping benzene rings, such as *para*-,[25] *meta*-[26] or multilayered cyclophanes.[27, 28] It should however be emphasized that a quantitative treatment of the individual chemical shifts is impossible in the absence of accurate X-ray diffraction measurements.[29]

Attention is drawn to the fact that in the helicene ($n \geqslant 6$), the most strongly shielded proton is always proton B and not proton A. Molecular models suggest that proton A is located in the vicinity of the axis of the helix and proton B approximately above the center of the adjacent underlying ring, that is in the region of maximum shielding effect. In addition, local anisotropic currents of both π and σ character[30] arising from the underlying ring (σ-bonds and π-orbitals) may contribute substantially to the observed chemical shifts.

* See Addenda 1.b and 2.

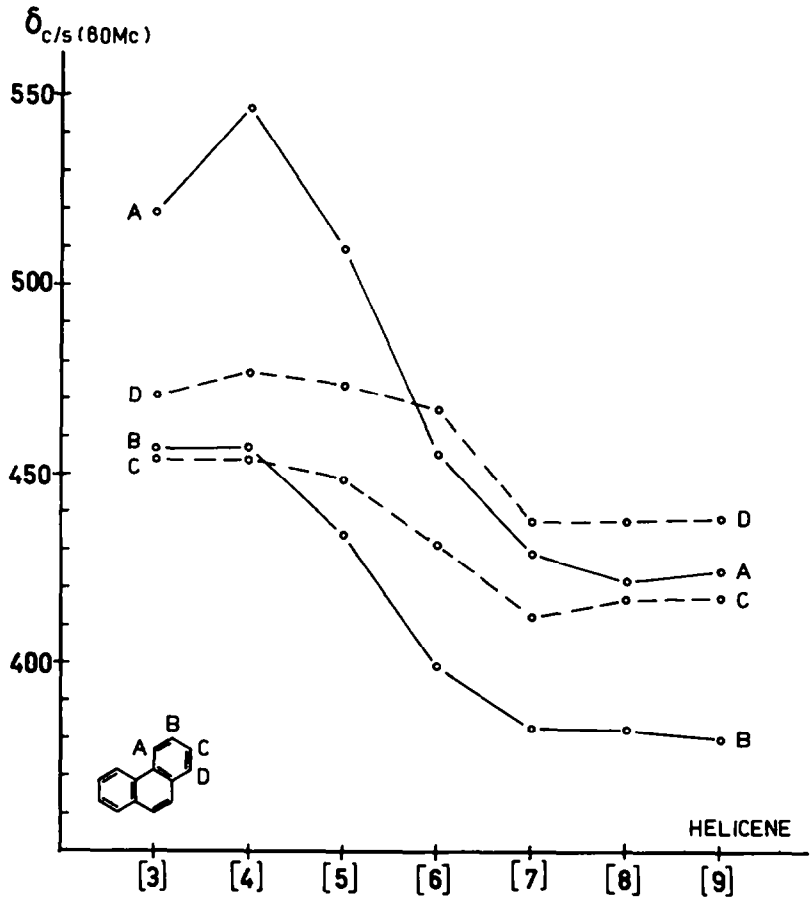


FIG. 7. Influence of the progressive overlap of benzene rings on the proton chemical shifts of the four spin systems (terminal rings). Solvent: $CDCl_3$ (60 Mc/s).

2—*Two spin systems.* The best illustration of the influence of the progressive angular annelation on proton chemical shifts in the helicene series comes out from the study of the two spin system (protons E to K) in hexa-, hepta-, octa- and nonahelicene (Fig. 8).

In these hydrocarbons, the protons which are not affected by the partial or complete overlap of benzene rings are respectively E, F, G, H in hexa-, G. H. I in hepta-, I, J in octa- and K in nonahelicene. The protons having an adjacent underlying ring [i.e. protons of the second ring in heptahelicene (EF), of the third ring in octahelicene (GH) and of the fourth ring in nonahelicene (IJ)] are shifted to higher fields, the effect being larger on the first proton of each pair. The protons located just under an overlapping end ring (EF in octahelicene and GH in nonahelicene) are shifted further to higher fields. In this case however the relative shielding effect is larger on the second proton of the pair.

These observations on the systematic and progressive shielding of the protons along the helix, by successive annelations, are in complete agreement with the expectations deduced from the study of molecular models. That the observed shieldings

cannot be ascribed to a constant decrease of the ring-currents in this series (e.g. by strong distortion of benzene rings) is confirmed by the following observations:

(a) The chemical shift of proton D remains fairly constant in I, II, III and IV.

(b) The singlet due to the protons of the central ring in the hydrocarbons containing an odd number of rings (I, III, V and VII) appears at lower fields in the higher benzologues: E in I at 462·1 c/s, G in III at 467·6 c/s, I in V at 477·7 c/s and K in VII at 476·6 c/s ($CDCl_3$ – 60 Mc/s).

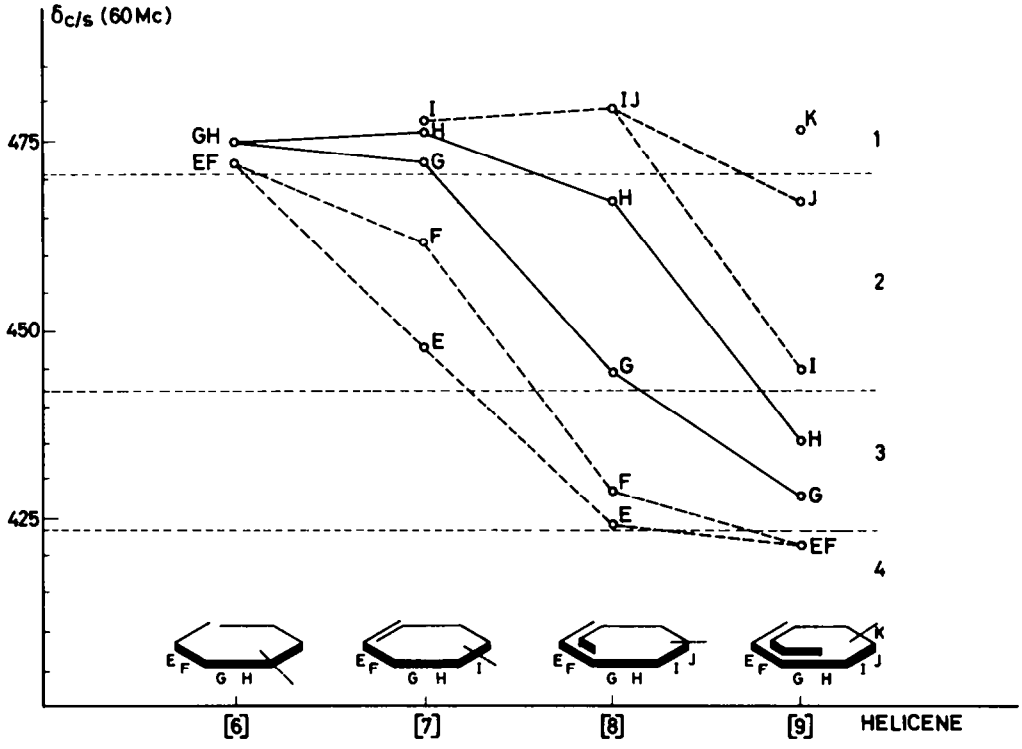


FIG. 8. Influence of the progressive overlap of benzene rings on the proton chemical shifts of the two spin systems. Solvent: $CDCl_3$ 60 Mc/s). Four regions:

1. "Unperturbed" protons.
2. Pair(s) of protons located just before an overlapping terminal-ring.
3. Pair(s) of protons located under an overlapping terminal-ring.
4. Pair(s) of protons located under a "non-terminal" overlapping-ring.

(b) *Specific solvent effects*

A change of solvent from chloroform to deuterated benzene produces in the case of planar polycyclic aromatic hydrocarbons an *upfield shift* of ca. 13 c/s of all the protons[1c] (see e.g. phenanthrene in Table 2). In the higher helicenes however, proton A undergoes a specific solvent effect which increases regularly from benzo[*c*]phenanthrene to hexahelicene and in this last molecule, a *downfield shift* of ca. 15 c/s is observed. The amplitude of this effect seems to be the same in the case of partial (hexahelicene) or complete (e.g. heptahelicene) overlap of the end rings.

It is clear from Table 2 that the protons B, C... G, H, also show this particular

TABLE 3. TEMPERATURE EFFECT ON THE NMR SPECTRUM OF HEXAHELICENE IN C_6D_6 SOLUTION

Conc.: 3% w/v
Values in c/s (60 Mc) of the center of the multiplet
Internal standard: hexamethyldisiloxane

T°	A	B	C	D	EF	GH
55°	460·5	383·1	412·5	450·7	454·4	456·3
34°	463·5	384·0	413·4	451·8	455·3	457·1
8°	469·5	385·0	414·2	452·8	456·3	458·0
$\Delta_{\nu 8}^{55}$	9·0	1·9	1·7	2·1	1·9	1·7

specific solvent effect as the number of overlapping rings increases in the helicene series.

Several authors have suggested that the upfield shift commonly encountered in benzene solution relative to chemical shifts measured in some magnetically "inert" solvents may be due to the fact that the shielding volume above and below the plane of the solvent (benzene) molecule is greater than the deshielding volume around the periphery which a solute (helicene) molecule can occupy.[31-33] Thus, after averaging over all possible molecular orientations, the net result is that the different protons of the solute are shielded by the aromatic solvent. The "anomalously" small solvent effect shown progressively by protons A, B, C, . . . H could then be explained by the fact that, in overcrowded hydrocarbons, the solvent can approach the overlapping rings from *one* side only, which is not the case for the internal reference T.M.S.

However, if these effects were due solely to the statistical number of solvent molecules which can shield the solute protons, then it would be hard to explain the specific increase in deshielding effect shown by proton A, relative to the other protons, in hexahelicene when the temperature is reduced (Table 3). Although "a slight structuring of the solvent about each solute molecule"[34] cannot be excluded, this last result suggests the formation of a weak complex bringing (a) benzene molecule(s) in a position simulating the "building up" of the helix. Interactions of this type between aromatic molecules have been indeed postulated recently.[35] Further work on this question is in progress.

CONCLUSIONS

This study fully confirms the structures attributed to the hydrocarbons described as hepta-, octa- and nonahelicene in our preliminary publications.[12, 13]

It further shows that the modifications of the NMR spectra of the helicenes, produced by progressive angular annelation, follow a constant trend, which can be interpreted qualitatively.

Acknowledgements—The authors are indebted to the following Belgian scientific Organisations: I.R.S.I.A., F.N.R.S. and F.R.F.C., for financial support. They also wish to thank Dr. P. Dedieu for assistance in the computer work involved, and Mr. R. Polain who recorded the N.M.R. spectra.

ADDENDA

1. After this paper was written, Bartle and Jones published a comprehensive study of the NMR spectrum of benzo[c]phenanthrene [K. D. Bartle and D. W. Jones, *J. Chem. Soc.* (A) 437 (1969)]. The results of this work, which includes the mathematical analysis of the system and the study of long range cross-ring couplings, specific solvent effects (CS_2-C_6D_6) and temperature changes, are in good agreement with our own findings.

Only on two points, do we wish to make a short comment:

a. We now have compiling evidence that cross-ring coupling between H_1 and H_{12} ($J_{1,12}$) are large enough to be observed in benzo[*c*]phenanthrene derivatives (to be published shortly). We therefore suggest that the long range cross-ring couplings of H_1 in benzo[*c*]phenanthrene itself is more likely to involve H_{12} than H_8 (these two hypotheses are considered by the authors).

b. Careful analysis of the sign of the discrepancies between the calculated (planar molecular model) and observed chemical shifts reported in Table 1 for benzo[*c*]phenanthrene provides evidence for an appreciable deshielding of proton A relative to its predicted theoretical position.

2. In a private communication, Mr. C. W. Haigh (University College, Swansea) has informed us that he and Mr. R. B. Mallion have also carried out experimental work on the PMR of non-planar condensed benzenoid hydrocarbons; and that they have developed a quantum-mechanical theory for the chemical shifts in these compounds.

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