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^{13}C-NMR SPECTROSCOPY IN THE HELICENE SERIES[1] : HEPTAHELICENE, HEXAHELICENE AND THE LOWER BENZOLOGUES.

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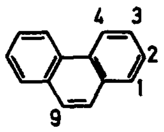
The ^{13}C-NMR spectra of naphthalene, phenanthrene (I), benzo[c]phenanthrene (II), pentahelicene(dibenzo[c,g]phenanthrene) (III), hexahelicene (IV) (Fig.1) and heptahelicene (V) (Fig.1) have been recorded on a Brucker HX high resolution spectrometer operating at 22.63 MHz and equipped with a broad band proton decoupler (90 MHz).



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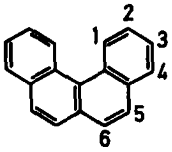

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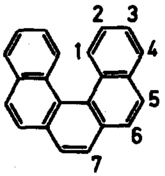

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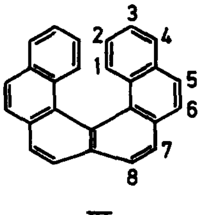

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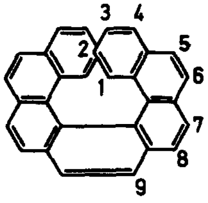

V

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[1] Part XVI of "Applications of NMR spectroscopy in the field of polycondensed aromatic compounds"; part XV, see ref. (1).

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Table 1 : ^{13}C-NMR spectra of the helicenes and lower benzologues

[7]helicene		[6]helicene		[5]helicene		benzo[c]phenanthrene		phenanthrene		naphthalene	
1.7:100[1]		2.5:100		2.5:100		2.5:100		2.5:100		2.5:100	
δ [2]	assign.	δ	assign.	δ	assign.	δ	assignment	δ	assign.[3]	δ	assign.[3]
54.8	Q[4]	55.9	8a or 16c	55.4	Q	56.3	4a or 12a	54.9	(8a)	56.3	4a
54.6	Q	54.6	Q	55.1	Q	53.8	6a or 12b	53.2	(4a)	50.5	1
53.6	Q	54.0	Q	53.6	Q	53.1	12a or 4a	51.3	1	48.5	2
52.3	Q	52.8	Q	51.8	1	51.3	4	49.6	9		
51.1	Q	50.8	Q	50.5	(5 or 4)	50.6	1	49.3	2,3		
50.2	7	50.5	(5)[5]	50.2	(4 or 5)	50.2	5,12b or 6a	45.4	4		
50.1	5	50.4	1	49.9	(7 or 6)	49.5	6				
49.5	8,9	50.2	4	49.8	Q	48.8	3 or 2				
49.4	4	49.9	7	49.0	(6 or 7)	48.5	2 or 3				
48.4	6	49.5	8	48.9	3						
48.1	Q	48.9	(6)	47.0	2						
47.7	3	48.2	3								
47.0	1	47.3	2								
46.4	2	46.8	16c or 8a								

[1] Hydrocarbon/$CHCl_3$ mol ratio.

[2] ppm downfield from $CHCl_3$; benzene δ = 51.1 ppm (mol ratio 2.5:100 in $CHCl_3$).

[3] ref. (2).

[4] Q = non protonated carbon atom.

[5] (   ) = provisional assignment.

The spectra were accumulated (100-400 scans) in a T.M.C. 1000 computer of average transients (CAT) with the field locked on the ^{19}F resonance of C_6F_6 at 84.6 MHz.

The sample tube (10 mm diam.) was fitted with a coaxial cell containing C_6F_6. The use of an external referent was imposed by the very low solubility of the polycyclic aromatic hydrocarbons in the presence of hexafluorobenzene.

The hydrocarbons were dissolved in $CHCl_3$ in mol ratios of 2.5-1.7:100, depending on their respective solubilities. The influence of dilution was tested on benzene, naphthalene, phenanthrene and benzo[c]phenanthrene. Deshieldings of the order of 0,1 to 0,2 ppm were observed when the solutions were diluted from 20:100 to 2,5:100 (mol ratios). The chemical shifts are expressed in ppm from the ^{13}C resonance of $CHCl_3$, with an accuracy of $\sim$ 0,1 ppm.

The noise off-resonance decoupling technique (NORD) (2), was used to distinguish the non protonated carbons from the other carbon atoms. The assignment of individual protonated carbon atoms was done by selective double resonance.

The results are collected in Table 1. The assignments given for naphthalene and phenanthrene are those reported by Alger, Grant and Paul (3).

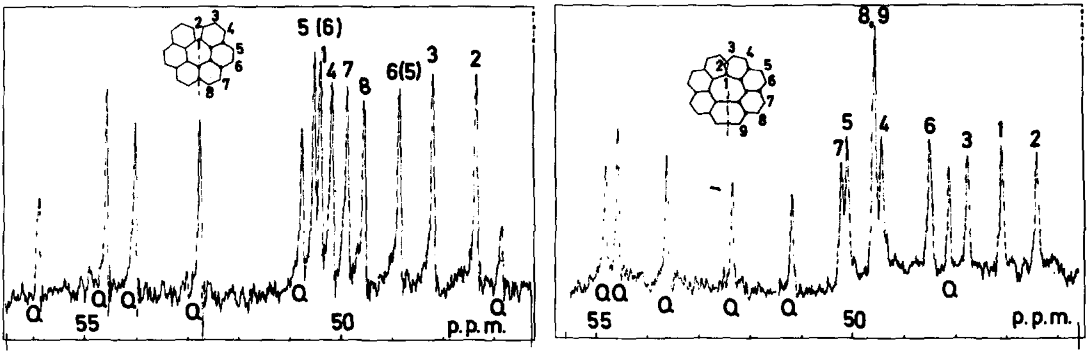

Fig. 1. Fully decoupled ^{13}C-NMR spectra of hexahelicene (145 scans) and heptahelicene (345 scans).

Protonated carbons.

Selective double resonance experiments, based on the fully analysed ^1H-NMR spectra described earlier (1), gave the following results:

- in heptahelicene, the protonated carbon atoms have all been assigned.
- in hexahelicene, both H_5-H_6 and H_7-H_8 give a singlet at 90 MHz. In order to differentiate the signals of $^{13}C_7$ and $^{13}C_8$, we have examined the ^{13}C-NMR spectrum of hexahelicene-7d$_1$, prepared previously (4). In the spectrum of this monodeuteriated helicene, the signal at 49.9 ppm is approximately half the size of the corresponding signal in the non deuteriated hydrocarbon.

- in pentahelicene, the selective double resonance experiments gave unambiguous results for $^{13}C_1$, $^{13}C_2$ and $^{13}C_3$ only.
- in benzo[c]phenanthrene, a choice between $^{13}C_2$ and $^{13}C_3$ was not possible.

Non protonated carbons.

The NORD technique was used to distinguish the non protonated carbons from the protonated carbon atoms. Amongst the signals due to the non protonated carbons, those corresponding to one carbon atom (C_{6a} and C_{12b} in benzo[c]phenanthrene and C_{8a} and C_{16c} in hexahelicene) can be distinguished from the signals corresponding to two identical carbon atoms. Much further work will be required to assign the individual non protonated carbon atoms.

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