¹³C-NMR SPECTROSCOPY: ISOTOPE SHIFTS AND COUPLINGS IN MONO- AND DIDEUTERIATED POLYCYCLIC AROMATIC HYDROCARBONS—XIX[a]

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Abstract—The deuterium isotope upfield shifts and couplings ($J_{^{13}C_\alpha-D}$ and $J_{^{13}C_\gamma-C-C-D}$) observed in the ¹³C-NMR spectra (22·63 MHz) of naphthalene-1-d, naphthalene-2-d, phenanthrene-9-d, benzo[c]phenanthrene-2-d, hexahelicene-7-d and anthracene-9,10-d₂ can be used to assign some of the following ¹³C-signals: ¹³C$_\alpha$-D, ¹³C$_\beta$-C-D *ortho*, ¹³C$_\gamma$-C-C-D *meta* (^3J_t) and ¹³C$_\gamma$-C-C-D *peri* (^3J_c). These isotope effects are particularly useful for the assignment of the signals of the carbon atoms common to two rings (quaternary carbon atoms, C_Q). The study of anthracene-9,10-d₂ has yielded results which are at variance with published assignments[2] concerning anthracene itself.

In the field of polycondensed benzenoid hydrocarbons, very little work has been done on isotope effects due to specific deuterium labelling in ¹³C-NMR spectroscopy.

In monodeuteriobenzene, Bell *et al.*[3] have observed the following "isotope upfield shifts" relative to benzene: ¹³C$_\alpha$-D (0·289 ppm), ¹³C$_\beta$-C-D *ortho* (0·110 ppm) and ¹³C$_\gamma$-C-C-D *meta* (0·011 ppm). Monosubstituted benzene derivatives, specifically labelled (D) in *ortho*, *meta* or *para*, show similar isotope effects.[3-5]

Deuteriodeprotonations have been studied successfully by ¹³C-NMR spectroscopy.[6,7]

The signal assignments of the ¹³C-NMR spectra of polycondensed aromatic hydrocarbons given by Lauterbur,[8] by Grant *et al.*[2,9-12] and by Martin *et al.*[13] were essentially based on noise off-resonance decoupling, selective double resonance and theoretical considerations.

Carbon atoms common to two rings (quaternary C atoms, C_Q) have been assigned by Grant *et al.* in alternant and non-alternant polycyclic aromatic hydrocarbons either on the basis of the relative amplitude of the nuclear Overhauser effect (NOE) observed for different sets of quaternary C atoms in a given hydrocarbon[11,12] or by the theoretical prediction of their relative chemical shifts.[9,12]

In the present study, we have examined the possibility of using specific deuterium labelling with the view to unambiguously assigning signals of C atoms which cannot be assigned by selective double resonance (e.g., quaternary C atoms) in the field of polycyclic aromatic hydrocarbons.

The results have been rather rewarding, for we have observed that the introduction of a single deuterium atom will in favorable cases, allow the assignment of a number of the following ¹³C-signals: ¹³C$_\alpha$-D, ¹³C$_\beta$-C-D *ortho*, ¹³C$_\gamma$-C-C-D *meta* (^3J_t) and ¹³C$_\gamma$-C-C-D *peri* (^3J_c).

RESULTS AND DISCUSSION

A preliminary investigation of the ¹³C-NMR spectra of the non-deuteriated polycyclic aromatic hydrocarbons studied in this work has already been published.[13] The data pertaining to the mono- and dideuteriated hydrocarbons (δ's ppm from TMS, and assignments) are collected in Table 1. The isotope effects produced by the deuterium atom(s) are summarised in Table 2. In this Table, the isotope shifts Δ_t's are expressed as the difference between the chemical shift of a given C atom in the deuteriated hydrocarbon and the chemical shift of either an equivalent C atom in the same molecule (internal reference) or the chemical shift of the same C atom in the non-deuteriated hydrocarbon ($\Delta_t = \delta_{(H)}^{13} - \delta_{(D)}^{13}$). In this last case, the spectra were recorded on a binary mixture of the deuteriated and non-deuteriated hydrocarbons.

The C atoms which are not included in Table 2 are indistinguishable under our recording conditions *vide infra*.

The deuterium isotope effect is characterised by the following upfield shifts and couplings:

(a) ¹³C$_\alpha$-D: Δ_t from +0·27 to +0·38 ppm. When the concentration of the deuteriated hydrocarbon is sufficient, the triplet of ¹³C$_\alpha$-D is clearly visible: $J_{^{13}C_\alpha-D} \sim 24·5$ Hz.

(b) ¹³C$_\beta$-C-D *ortho*: Δ_t from +0·05 to +0·12 ppm. When two *ortho* C atoms (¹³C$_\beta$-CD-¹³C$_\beta$) are present, the corresponding Δ_t's may be appreci-

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XVIII, see Ref 1.

Table 1. ^{13}C-NMR spectra of specifically deuteriated aromatic hydrocarbons

Naphthalene-1-d (1)		Naphthalene-2-d (2)		Anthracene-9,10-d₂ (6)		Phenanthrene-9-d (3)		Benzo[c]phenanthrene-2-d (4)		[6]Helicene-7-d (5)	
20:100[a]		20:100		2:100		20:100		7:100		0·6:100	
δ[b]	assign.	δ	assign.	δ	assign.	δ	assign.	δ	assign.	δ	assign.
125·69	2	125·55	2	125·38	2, 3, 6, 7	122·64	4, 5	125·73	3	124·20	16c or 8a
125·81	3, 6, 7	125·75	3	125·87	9, 10	126·49	2, 3, 6, 7	125·83	10	124·74	2, 15
127·58	1	125·83	6, 7	128·17	1, 4, 5, 8	126·55	9	125·85	2	125·59	3, 14
127·89	4, 5, 8	127·83	1	131·70	4a, 10a 8a, 9a	126·75	10	126·12	11	126·18	6
133·48	8a	127·95	4, 5, 8			128·48	8	126·85	6, 7	126·23	11
133·55	4a	133·53	4a, 8a			128·52	1	127·40	12b or 6a	126·83	8
						130·32	4a, 4b	127·47	5, 8	126·93	9
						131·99	8a	127·79	1	127·28	10
						132·05	10a	127·90	12	127·57	4, 13
								128·57	4, 9	127·76	1, 16
								130·38	12a, 12c	127·93	5, 12
								131·06	6a or 12b	128·11	Q[c]
								133·57	4a, 8a	129·99	Q
										131·27	6a
										131·32	10a
										131·85	Q
										133·20	8a or 16c

[a] Hydrocarbon/CHCl₃ mole ratio.
[b] ppm downfield from TMS; ± 0·02 ppm.
[c] Q = carbon atom common to two rings.

Table 2. Deuterium isotope effects

Deuteriated hydrocarbon	$^{13}C_\alpha$-D			$^{13}C_\beta$-C-D *ortho*		$^{13}C_\gamma$-C-C-D *meta*		$^{13}C_\gamma$-C-C-D *peri*		
	^1J(Hz)	Δ_i[b]	assign.	Δ_i	assign.	$\nu 1/2$[c]	assign.	$\nu 1/2$	Δ_i	assign.
Benzene-d[a]	—	0·289	1	0·110	2, 6	($^3J_i = 1·14$ Hz)	3, 5			
Naphthalene-1-d (1)	24·4	0·31	1	0·12	2	2·3	4a			
				0·07	8a					
Naphthalene-2-d (2)	24·5	0·28	2	0·12	1	—	8a[d]			
				0·08	3					
Phenanthrene-9-d (3)	24·5	0·31	9	0·12	10	3·0	10a	2·3	0·04	8
				0·07	8a					
Benzo[c]phenanthrene-2-d (4)	24·5	0·27	2	0·11	1	—	4[d]			
				0·10	3	—	12c[d]			
Hexahelicene-7-d (5)	—	—	7	0·10	8			2·0	0·05	6
				0·05	6a					
Anthracene-9,10-d₂ (6)	24·8	0·38	9, 10	0·09	4a, 8a 9a, 10a	2·3	4a, 8a 9a, 10a	2·0	0·04	1, 4 5, 8

[a] See Ref 3.
[b] $\Delta_i^{ppm} = \delta_{CH}^{13C} - \delta_{CD}^{13C}$.
[c] $\nu 1/2$ = width at half-height (Hz); $\nu 1/2 \simeq 1$ Hz for the ^{13}C located anywhere but in *meta* and *peri* to the D.
[d] Assignment based on the low intensity of the signal.

ably different. In a given hydrocarbon, the larger one is associated with the larger π-bond order.[*] In monodeuteriobenzene, the *ortho* coupling (^2J) can be estimated ($|J_{^{13}\text{C-D}}| = |J_{^{13}\text{C-H}}|/6·5$) to be of the order of 0·15 Hz on the basis of the corresponding coupling ($J_{^{13}C_\beta\text{-C-H}} = 1·0$ HZ) observed in benzene itself by Weigert and Roberts.[14]

(c) $^{13}C_\gamma$-C-C-D *meta*. No isotope shift has been observed on *meta* C atoms but band-broadenings due to *meta* couplings (^3J_i) are clearly visible. In monodeuteriobenzene, Bell *et al.*[3] have "shown"

*For correlations between π-bond orders and bond lengths *cf* Refs 20 and 21.

that $J_{^{13}C_\gamma\text{-}C\text{-}D} = 1\cdot14$ Hz. This result is fully consistent with the value found in benzene itself: $J_{^{13}C_\gamma\text{-}C\text{-}C\text{-}H} = 7\cdot4$ Hz.[14] A similar band-broadening in *meta* is also observed in the ¹³C-NMR spectrum of benzonitrile-2-d.[5]

(d) $^{13}C_\gamma$-C-C-D *peri*: $\Delta_i \sim 0\cdot04$ ppm. It is interesting to note that band-broadenings, apparently due to *peri* couplings (^3J_c) are observed.

The results obtained so far clearly show that specific deuterium labelling can be of great help in the analysis of the ¹³C-NMR spectra of polycyclic aromatic hydrocarbons, not only for the assignment of the $^{13}C_\alpha$-D C atom but also for the *ortho, meta* and *peri* C atoms. In particular, this technique appears to be the simplest and the most reliable one for the assignment of the C atoms common to two rings. Inspection of Table 2 shows that the magnitude of the *ortho* high field deuterium isotope shifts of these C atoms (C_O) is of the order of 0·05 to 0·09 ppm.

Naphthalene-1-*d* (**1**) *and naphthalene*-2-*d* (**2**). The ¹³C-NMR spectrum of naphthalene has been fully assigned by Grant *et al.*[9]

Ortho effect. In naphthalene-2-d, the *ortho* deuterium upfield shifts and the corresponding π-bond orders ($p_{r,s}$) are respectively: $^{13}C_1$: $\Delta_i = 0\cdot12$ ppm, $p_{1,2} = 0\cdot725$ and $^{13}C_3$: $\Delta_i = 0\cdot08$ ppm, $p_{2,3} = 0\cdot603$.

Phenanthrene-9-*d* (**3**). The ¹³C-NMR spectrum of phenanthrene has been fully analysed by Grant *et al.*[9] In phenanthrene-9-d (Fig 1), the *ortho* effects and π-bonds orders are respectively: $^{13}C_{10}$: $\Delta_i = 0\cdot12$ ppm; $p_{9,10} = 0\cdot775$ and $^{13}C_{8a}$: $\Delta_i = 0\cdot07$ ppm; $p_{8a,9} = 0\cdot506$.

Our assignment of the quaternary C atoms fully agrees with the previous assignment of Grant *et al.*[9] Their assignments of $^{13}C_1$ and $^{13}C_9$ are also confirmed. It is interesting to note that the *peri* C atom $^{13}C_8$ shows a $\Delta_i = 0\cdot04$ ppm (relative to $^{13}C_1$). The

signal of $^{13}C_8$ shows an unresolved coupling ($\nu_{1/2} = 2\cdot3$ Hz).

The *meta* coupling of the quaternary C atom $^{13}C_{10a}$ is apparent in its lower intensity and enhanced band width ($\nu1/2 = 3\cdot0$ Hz *vs* 1·0 Hz in phenanthrene).

Benzo[c]*phenanthrene*-2-*d* (**4**). A preliminary study of the ¹³C-NMR spectrum of benzo[c]phenanthrene was reported earlier.[13] It should be pointed out that in a new spectrum (Fig 2) of benzo[c]-phenanthrene recorded in CHCl₃ (7 : 100 mole ratio) by Fourier transform, the signals of $^{13}C_{6a}$ or $^{13}C_{12b}$ on the one hand and $^{13}C_5 + ^{13}C_8$ on the other hand, are well resolved ($\delta = 127\cdot40$ and $127\cdot47$ ppm, respectively).

In the present work, specific deuterium labelling in position 2 (Fig 2) has allowed us to distinguish $^{13}C_2$ from $^{13}C_3$ and to confirm the assignment of $^{13}C_1$. *Meta* couplings are responsible of the band-broadening of $^{13}C_4$ and of the signal of the quaternary C atom located at 130·38 ppm, which can thus be assigned to $^{13}C_{12c}$. The only problem left is the unambiguous assignment of $^{13}C_{6a}$ and $^{13}C_{12b}$. This could easily be done by specific deuterium labelling in position 6.

Hexahelicene-7-*d* (**5**).[15] The ¹³C-NMR spectra of hexahelicene and hexahelicene-7-d have been described in a previous communication.[13] The signals of the protonated C atoms were all assigned, but those of $^{13}C_5$ and $^{13}C_6$. On the other hand, no quaternary C atom was individually assigned, although $^{13}C_{8a}$ and $^{13}C_{16c}$ could be distinguished from the other eight quaternary C atoms. The isotope effects described above have now been used to unambiguously assign $^{13}C_{6a}$ (*ortho* effect) and $^{13}C_6$ (*peri* effect) and to confirm the assignment of $^{13}C_8$ (*ortho* effect). The small amount of material at our disposal prevented us from taking advantage of the *meta* couplings in order to locate $^{13}C_{8a}$ and $^{13}C_{16d}$. Specific
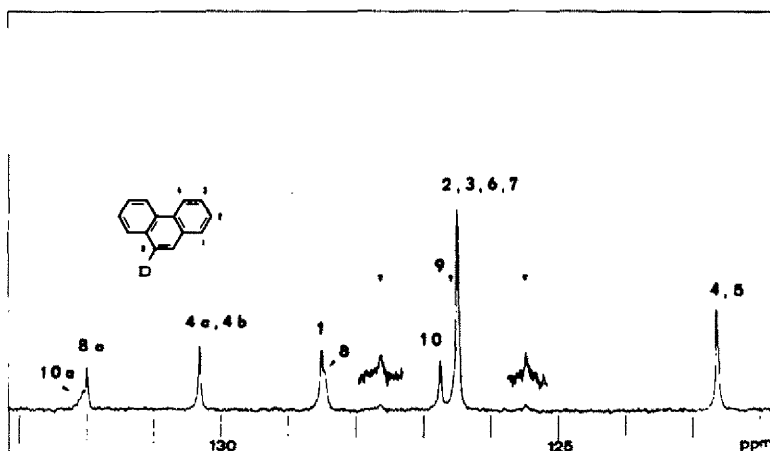

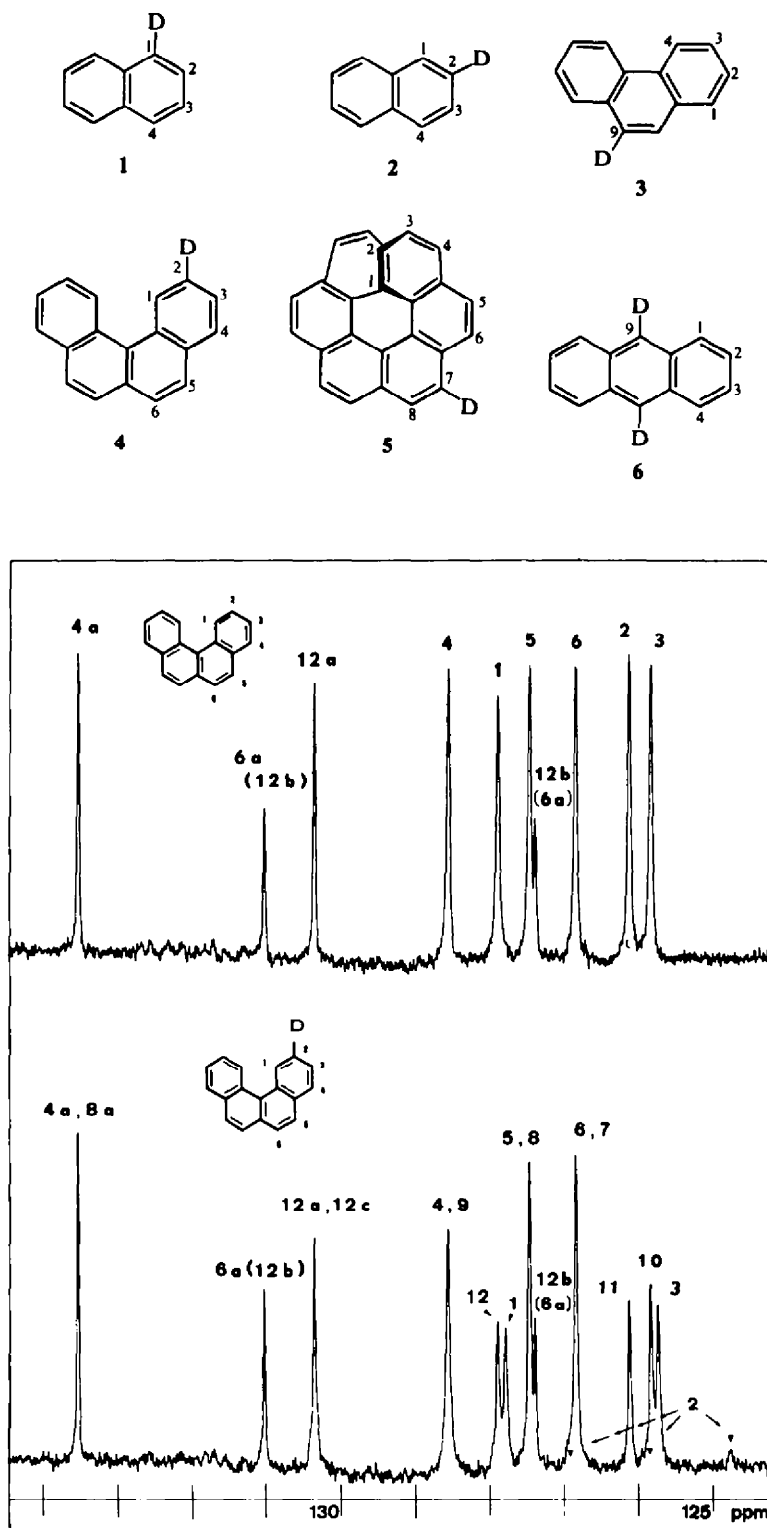Fig 1. Fully decoupled ¹³C-NMR spectrum of phenanthrene-9-d (F.T. 957 scans).

Fig 2. Fully decoupled ^{13}C-NMR spectra of benzo[c]phenanthrene (F.T. 2400 scans) and benzo[c]phenanthrene-2-d (F.T. 2642 scans).

deuterium labellings in positions 1, 4 (or 5) and 8 would allow the complete assignment of the remaining quaternary carbon atoms in hexahelicene.

Anthracene-9,10-d_2 (6). The ^{13}C-NMR spectrum of anthracene (sat soln in benzene) has been analysed by Grant *et al.*[2] We have ourself analysed the spectrum of this hydrocarbon in sat C_6D_6 and CHCl$_3$ solns. Our assignments are based on noise off-resonance decoupling and selective double resonance experiments. The results of the two laboratories are collected in Table 3.

Table 3. ^{13}C-NMR spectra of anthracene

Grant *et al.*[a]		This work[b]	
$\delta(C_6H_6)$	Assignments	δ(CHCl$_3$)	$\delta(C_6D_6)$
132·59	C$_9$	126·28	126·74
132·27	C$_{4a}$	131·81	132·32
130·13	C$_1$	128·23	128·58
125·55	C$_2$	125·40	125·56

[a] In the original publication,[2] the δ's were given by reference to benzene. We have expressed them by reference to TMS using the following equation:

$$\delta^{ppm}_{TMS} = \delta^{ppm}_{C_6H_6} + 128·53.^{16}$$

[b] ppm downfield from TMS.

In view of the discrepancies between our assignments and those of Grant *et al.*,[2] we have examined the ^{13}C-NMR spectra of anthracene-9,10-d_2 and of a binary mixture of anthracene-9,10-d_2 and anthracene in sat C_6D_6 and CHCl$_3$ solns. Apart from the triplet of the deuteriated *meso* C atoms (^{13}C$_{9\ and\ 10}$), *ortho* ^{13}C$_{4a,10a,8a\ and\ 9a}$) and *peri* (^{13}C$_{1,4,5\ and\ 8}$)

isotope shifts are clearly visible. The signals of the *ortho* and *peri* C atoms are moreover broader than the signal of ^{13}C$_{2,3,6,7}$ on account of *meta* and *peri* couplings: $\nu 1/2$ ^{13}C$_2 = 1$ Hz; $\nu 1/2$ ^{13}C$_1 = 2$ Hz; $\nu 1/2$ ^{13}C$_{4a} = 2$ Hz.

This study of deuterium isotope effects fully confirms our interpretation of the ^{13}C-NMR spectrum of anthracene.

1-Bromonaphthalene and 9-bromophenanthrene. In the course of this work, we have also recorded the ^{13}C-NMR spectra of 1-bromonaphthalene and 9-bromophenanthrene and have assigned some of the signals by noise off-resonance decoupling and selective double resonance (*cf* Table 4). It is significant to note that in these monosubstituted hydrocarbons, *all the carbon atoms are anisochronous*.

Spiesecke and Schneider[17] who have analysed the ^{13}C-NMR spectrum of bromobenzene have observed a high field shift, relative to benzene, of + 5·4 ppm for the ^{13}C$_a$-Br C atom and low field shifts of the *ortho* (− 3·3 ppm) and *meta* (− 2·2 ppm) C atoms. It is therefore highly reasonable to assign the signal at 122·78 ppm in 1-bromonaphthalene to ^{13}C$_1$ (+ 5·0 ppm) and the signals at 121·55 ppm and 130·30 ppm in 9-bromophenanthrene to ^{13}C$_9$ (+ 5·3 ppm) and ^{13}C$_{10}$ (− 3·4 ppm) respectively. The high field shifts of the C atoms *peri* to the Br atoms are relatively small: + 0·7 ppm in 1-bromonaphthalene and + 0·8 ppm in 9-bromophenanthrene.

EXPERIMENTAL

^{13}C-NMR *spectra.* The ^{13}C-NMR spectra were recorded on a Brucker HX 90 high resolution spectrometer operat-

Table 4. ^{13}C-NMR spectra of monobrominated aromatic hydrocarbons

Bromobenzene[17]			1-Bromonaphthalene			9-Bromophenanthrene		
			20:100[b]			20:100		
δ[a]	assign.	Δ_{Br}[e]	δ[c]	assign.	Δ_{Br}	δ[c]	assign.	Δ_{Br}
123·13	1	+ 5·4	122·78	1	+ 5·0	121·55	9	+ 5·3
131·83	2, 6	− 3·3	126·10			122·43	4 or 5	
130·73	3, 5	− 2·2	126·65			122·52	5 or 4	
127·53	4	+ 1·0	127·06	8	+ 0·7	125·86		
			127·23			126·88		
			127·88			127·11		
			128·29			127·19		
			129·87			127·52		
			132·01	Q[d]		127·77	8	+ 0·8
			134·66	Q		129·46	Q	
						130·09	Q	
						130·30	10	− 3·4
						131·00	Q	
						131·91	Q	

[a] *cf* foot-note *a* Table 3.
[b] Hydrocarbon/CHCl$_3$ mole ratio.
[c] ppm downfield from TMS.
[d] Q = C atom common to two rings.
[e] $\Delta^{ppm}_{Br} = \delta^{13C}_{(H)} - \delta^{13C}_{(Br)}$.

ing at 22·63 MHz with the field locked on the ^{19}F resonance of C_6F_6 at 84·6 MHz and equipped with a broad band proton decoupler (90 MHz). The sample tube (10 mm diam) was fitted with a coaxial cell containing C_6F_6. The products were dissolved in CHCl$_3$ (internal reference) in mole ratios of 20–0·6 : 100 depending on their solubilities or availability. The chemical shifts are expressed in ppm with reference to the ^{13}C resonance of TMS using the following equation: $\delta_{TMS}^{ppm} = \delta_{CHCl_3}^{ppm} + 77·30$ ppm. Positive values correspond to low field shifts.

The ^{13}C-NMR spectrum of naphthalene-2-d was accumulated (185 scans; 3 Hz/cm) in a TMC 1000 computer of average transients (CAT). The other spectra were obtained by the pulse Fourier transform mode (8K/4K; 600 Hz spectral window).

Syntheses

cis *and* trans 1-(p-*Bromophenyl*)-2-(2-*naphthyl*)-*ethylene*. A 5% excess of NaOCH$_3$ was added in an atmosphere of N$_2$ to a soln of β-naphthaldehyde (1·21 g; 7·8 mM) and 4-bromo-triphenylphosphoniomethylbenzene bromide (4 g; 7·8 mM) in anhyd MeOH (35 ml) and the mixture was stirred 16 h at room temp. The white ppt (0·94 g *cis + trans*) was collected and washed with ice cold MeOH. The soln was evaporated to dryness and chromatographed (alumina–petroleum ether 60–70°) giving 0·6 g (*cis + trans*), total yield: 64% (1·52 g). *Cis*-1-(p-Bromophenyl) - 2 - (2 - naphthyl) ethylene crystallised from MeOH, m.p. 73–74°. M$^+$: 308 and 310.

2 - *Bromobenzo* [c] *phenanthrene*. A soln of *cis + trans* 1 - (p - bromophenyl) - 2 - (2 - naphthyl) ethylene (0·87 g; 2·8 mM) in cyclohexane (950 ml) containing 34 mg of I$_2$ (0·1 mM) was photolysed for 2 h with a Hanovia 450 W medium pressure Hg lamp (pyrex well). The photocyclisation was followed by TLC on silica gel impregnated with 2, 4, 7 - trinitrofluorenone (benzene/petroleum ether 1 : 1). The reaction product was chromatographed on a column of silica gel with petroleum ether 60–70°. 2 - Bromobenzo [c] phenanthrene crystallised from MeOH in white needles, m.p. 86–87·5°. M$^+$: 306 and 308.

Deuteriodebromination

General procedure. The deuteriodebrominations were carried out by the general procedure described by Leitch *et al.*[18]

A suspension of the bromo derivative (10 mM), CaO (prepared by heating Ca(OH)$_2$ at 850° for 5 h; 3 g) Zn powder (30 g, washed successively with EtOH and ether and dried under reduced pressure in the reaction flask) in

Table 6. Isotopic purity of the deuteriated hydrocarbons

Deuteriated hydrocarbon	% d$_2$	% d$_1$	No deuterium (%)
1	—	99	1
2	—	96	4
3	—	98·5	1·5
4	—	93	7
6	98	2	—

20–30 ml of D$_2$O (99·8%D) and 1–2 ml benzene (to prevent sublimation of the bromo derivative) was vigorously refluxed, in an atmosphere of N$_2$, for a couple of days. The mixture, cooled in an ice-bath, was treated with CHCl$_3$ and aq HCl. When the Zn had completely reacted, the CHCl$_3$ layer was decanted, washed successively with H$_2$O, 10% Na$_2$CO$_3$, water and dried over MgSO$_4$. The deuteriated hydrocarbon was purified either by sublimation under reduced pressure (naphthalene-1-d, naphthalene-2-d and phenanthrene-9-d), by chromatography on alumina–petroleum ether 60–70° (benzo[c]phenanthrene-2-d) or by crystallisation from EtOH (anthracene-9,10-d$_2$).

The purity of the brominated and deuteriated hydrocarbons was controlled by GLC (4% or 10% OV$_1$ on Gaschrom Q) and by TLC (silica gel, petroleum ether 60–70°). The results are collected in Table 5. The deuterium isotope purity (*cf* Table 6) was determined by mass spectrometry (Hitachi Perkin Elmer RMU-6D) at low potential ($\sim$ 10 eV).

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Table 5. Deuteriodebrominations

Starting material	Reaction time	Deuteriated hydrocarbon	Yield %	m.p. (uncorrected)
1-Bromo-naphthalene	90 h	1	85% lit.[19]: 70%	81–81·5° (EtOH)
2-Bromo-naphthalene	88 h	2	83%	80–80·5°
9-Bromo-phenanthrene	115 h	3	98% lit.[18]: 45%	101–101·5°
2-Bromobenzo[c] phenanthrene	108 h	4	99%	66–67°
9,10-Dibromo-anthracene	156 h	6	100%	216–216·5° (EtOH)

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