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LONG-RANGE SPIN–SPIN COUPLING IN POLYCYCLIC HYDROCARBONS AND THEIR DERIVATIVES

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Abstract—Long-range spin–spin couplings have been derived from 60 and 100 Mc/s nuclear magnetic resonance spectra of 9 parent polycyclic hydrocarbons and 26 of their derivatives. Double-resonance experiments were carried out on the following compounds: anthracene (parent, 9-bromo-, and 9-methyl-derivatives); phenanthrene (parent, 1-methyl-, 1-methyl-7-isopropyl-, 3-acetyl-9,10-dimethyl-, 3-acetyl-9-bromo-, 2,7-dimethyl-, 3,6-dimethyl-, 9-methyl-, 9-fluoro-, 9,10 dihydro-, 9-formyl, and 2,2,2-, trimethoxy-4,5-(2,2'-biphenyleno)-1,3,2-dioxaphospholene); triphenylene (parent, 2-methyl-, 1,3-,2,3- and 2,7-dimethyl-, 2,3-dimethoxy-, 1,6,11-, and benz[*a*]anthracene (parent, 7-methyl-, and 7,12-dimethyl-derivatives); 1-methylpyrene; benzo[*c*]phenanthrene; dibenzo[*c*,*g*]phenanthrene; and fluorene. Measured values of coupling constants are tabulated as benzylic (*ortho*, *meta*, *para*, or aldehydic) or inter-ring (epi, bay, or peri).

A seven-bond methyl-methyl coupling is reported in 7,12-dimethylbenz[*a*]anthracene (estimated at 0·6 c/s) and also in *para*-methyl-benzylbromide (estimated at 0·4 c/s).

THE AROMATIC regions in the single-resonance high-resolution nuclear magnetic resonance (NMR) spectra of many polycyclic aromatic hydrocarbons and their derivatives display lines which are broadened or have small splittings between them. Assignment of these effects to spin-spin couplings, either between protons on different benzenoid rings or between aromatic protons and those of substituent alkyl groups, has often been at least partly intuitive, in contrast to the more specific attributions possible in heterocyclic systems. In this study, which forms part of our programme on the NMR spectroscopy and carcinogenic activity[12] of polycyclics[1–10] and their analogues,[11] the aim is to investigate these couplings and, where necessary, to establish their identity by the double-irradiation technique.[13, 14]

While coupling between aromatic protons on different rings of polynuclear hydrocarbons has generally been assumed to have negligible effect on the analyses of NMR spectra,[3,4,15–20] its occurrence has been suspected in a number of polynuclears. Thus broadenings of the AA' regions of the spectra of naphthalene[16] (I), triphenylene (II: R = H),[3,16] and 2,7-dimethyltriphenylene[3] (II: R = CH_3); and of the AA' and X peaks of anthracene (III),[16] as compared with other lines in the same spectra, have been attributed to unresolved inter-ring coupling.[2,25–28] The same explanation has been given tentatively[4] for broadening of the H(9,10) singlet and the H(4,5) multiplet in the spectrum of phenanthrene[4,21] (IV). Broadenings have also been observed for several regions, particularly the H(7) and H(12) singlets[18] of the benz [*a*]anthracene (V) spectrum,[20,22,23] and of the bay-proton resonances H(1,12) in benzo[*c*]phenanthrene[10] (VI) and H(1,14) in dibenzo[*c*,*g*]phenanthrene[24] (VII).

Some of the attributions to inter-ring coupling are based on analogy with well-documented[29–33] inter-ring coupling in the corresponding heterocycles; most of the

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others involve comparison with derivatives which show clearer or resolvable splitting or else exhibit significant narrowing of appropriate signals in comparison with the parent.[4] The confirmation by spin-decoupling[7] of the H(1)—H(12) and H(7,12)—H(8,11) couplings in the non-alternant hydrocarbon benzo[*k*]fluoranthene (VIII), which shows broadened H(1,6), H(7,12), and H(8,11) lines, represents one of the few applications of the double-resonance technique to this problem to date.

Short spin-lattice relaxation times for the sterically hindered protons of polynuclear hydrocarbons (e.g. H(4,5) of IV) have been suggested[21, 10] as an alternative explanation of line broadening. Such a mechanism would be analogous to the efficient mutual relaxation, demonstrated by Anet *et al.* in IX,[34] which broadens the resonances of the close protons H_a and H_b.

Couplings between aromatic and side-chain protons have been most thoroughly studied in the mono-[29, 30, 35–46] and heterocyclic[30, 38, 47–49] series, but there have been a number of extensions to polycyclic systems, notably acenaphthene[50] and methylnaphthalenes,[51] -phenanthrenes,[4] -pyrenes[52] -benzo[*p*,*q*,*r*]perylenes,[53] -benzanthrones[51] and -coronene.[52] Because of the much larger differences between the chemical shifts of protons involved, benzylic coupling tends to be better documented than inter-ring coupling.

RESULTS AND DISCUSSION

In this study, the parent hydrocarbon and/or its derivatives have been examined for the following series: anthracene, phenanthrene, triphenylene, benz[*a*]anthracene, benzo[*c*]phenanthrene, pyrene, dibenzo[*c*,*g*]phenanthrene, benzo[*k*]fluoranthene, and fluorene. Among the tetracyclic hydrocarbons, chrysene and naphthacene were excluded owing to poor solubility and the lower signal-to-noise ratio possible in our double-irradiation experiments.

For many of the compounds discussed here, absence of actual line splittings as distinct from broadenings prevented direct measurement of the coupling. In such cases, we have followed Harris and Cunliffe[56] in attempting to estimate the true separation, J, of absorption lines, within an unresolved band of width at half-height Δ, from plots of J/Δ_0 v. Δ/Δ_0, where Δ_0 is the width of a single line (Figure 1). Band shape was assumed to depend only on overlap; Lorentzian envelopes[57] were calculated for symmetrical doublets, 1·2·1 triplets, and 1·3·3·1 quartets, with J between 0·1 and 0·7 c/s, and Δ between 0·3 and 1·0 c/s. Coupling constants are given in Table 1.

Anthracene and its derivatives

Field-sweep double-resonance experiments on a saturated solution of (III) in CS_2 confirmed coupling between the X and AA′ protons: irradiation at the H(9,10), or X, frequency sharpened each H(1,4) (AA′) peak so that Δ became the same as for the corresponding H(2,3) line. Correspondingly, Δ for the H(9,10) singlet decreased from 1·7 c/s to 1 c/s on irradiating at ν_A. Either peri [H(1)—H(9)] or epi [H(1)—H(10)] inter-ring coupling (or both) is consistent with these observations.

9-Bromoanthracene showed a typical ABMX spectrum (in $CDCl_3$ solution), with the broad H(10) signal immediately to high-field of the lowest-field H(1) group. Extra splittings were evident in both the latter and H(4) group; double-irradiation at the H(10) frequency showed that these arise from H(1)—H(10) and H(4)—H(10) coupling. Comparison of decoupled and normal spectra allowed measurement of

$J_{1,10} = J_{8,10} = 1{\cdot}0$ c/s, and $J_{4,10} = J_{5,10} = 0{\cdot}6$ c/s. Double irradiation is not possible in 9-methylanthracene ($CDCl_3$), because the H(10) signal is superposed on H(1), but again both H(1) and H(4) showed extra splittings; here $J_{1,10} = J_{8,10} = 1{\cdot}1$ c/s. Narayanan and Venkatasubramian claimed[58] that the 9-C$\underline{H}_3$ resonance is singlet. We find a doublet, $J = 0{\cdot}75$ c/s, which was shown by decoupling to arise from splitting by the *para* H(10).

Phenanthrene and its derivatives.

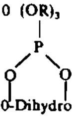
Fahey and Graham reported no significant narrowing of H(4,5) lines in phenanthrene when the H(9,10) resonance was irradiated.[21] However, in our field-sweep experiments in acetone, a solvent which gives greater shift differences than less polar solvents,[4] the highest-field phenanthrene H(4,5) lines were found to sharpen if the irradiating frequency-difference was exactly equal to the separation between the line in question and the H(9,10) singlet. Comparable observations were not possible for the lower-field lines, no doubt because of the close similarity between the difference and ν_3–ν_4; the appearance of the H(4,5) multiplet changed completely. Working from Fig. 1, the H(9,10) linewidth corresponds to $J_{4,10} = 0{\cdot}4$ c/s.

Confirmatory evidence that the H(4,5) signals of phenanthrene are broadened by long-range coupling rather than by a relaxation mechanism is provided by the constant line-width of both H(4,5) and H(1,8) lines between −55° and +124°; measurements in the range −55° to +35° were made in CS_2, and above +35° in $(CD_3)_2SO$. Anet *et al* found[34] that the widths of the H_a and H_b lines in IX became even larger at −60 .

In 1-methyl- and 1-methyl-7-isopropylphenanthrenes,[4] the identity of the 0·6 c/s long-range coupling of H(10) was confirmed; irradiation at the H(4) frequency caused the H(10) 0·6 c/s doublets to collapse to singlets. Similarly, the H(4)—H(5) coupling, suggested as the origin of small splittings observed[4, 5] in 9,10-dimethyl-, 9,10-diethyl-, and 9,10-dibromophenanthrenes (0·3 c/s, Fig. 2), and 9-t-butyl- and 9-*t*-pentylphenanthrenes (0·4 c/s), was positively identified in 3-acetyl-9,10-dimethylphenanthrene; irradiation of H(5) allowed resolution of the broadened H(4) signal as an apparent triplet in CS_2, and as a more deeply split doublet in $CDCl_3$. The reverse experiment (in $CDCl_3$) sharpened the H(5) lines. Finally, the occurrence of both H(4)—H(10) and H(4)—H(5) coupling in the same molecule—3-acetyl-9-bromophenanthrene in $CDCl_3$ solution—has been demonstrated: irradiation of H(4) narrowed H(5) lines and *vice versa*; H(10) and H(2) signals overlap but irradiation at the H(4) frequency produced sharp lines for both.

Bartle and Smith accounted[4] for Δ of the C$\underline{H}_3$ signals of 2,7-and 3,6-dimethylphenanthrenes in terms of *ortho* benzylic coupling. Spin-decoupling (CS_2 solution) confirms these, and also reveals small couplings of methyl to *meta* protons; H(4) and H(1) resonances respectively are narrowed on irradiation at the C$\underline{H}_3$ line. Thus, H(1) signals in 3,6-dimethylphenanthrene are now resolved as a pair of 0·5 c/s doublets; Fig. 1(c) suggests $J_{CH_3-H(1)} = 0{\cdot}2$ c/s. The much larger coupling of the CH_3 protons in 9-methylphenanthrene (1·1,[4, 52] 1·05 ± 0·05 c/s[38]) is directed to the *ortho* H(10), as we have confirmed by double-irradiation. We note, however, that the aldehydic proton resonance in 9-formylphenanthrene is a sharp singlet (Δ = 0·5 c/s). Although the P^{31} chemical shift of 2,2,2-trimethoxy-4,5-(2′,2′-biphenyleno)-1,3,2-dioxaphospholene[59–62] (XI: R = Me), the 1:1 adduct of trimethyl phosphite

TABLE 1. LONG-RANGE COUPLINGS IN

Series	Derivative	Inter-ring coupling							
		Identity	Magnitude (c/s)	Type	Bonds	Confirmed by DR	Measurement		Identity
							Direct	Indirect	
Anthracene	Parent	H(1)—H(9)		peri	4	√			
		and/or H(1)—H(10)		epi	5	√			
	9-Bromo	H(4)—H(10)	0·6	peri	4	√	√		
		H(1)—H(10)	1·0	epi	5	√	√		
	9-Methyl	H(1)—H(10)	1·1	epi	5	√	√		CH_3—H(10)
Phenanthrene	Parent	H(4) H(10)	0·4	epi	5	√*		√	
	1-Methyl	H(4)—H(10)	0·6	epi	5	√	√		
	1-Methyl-7-Isopropyl	H(4)—H(10)	0·6	epi	5	√	√		
	3-Acetyl-9,10-Dimethyl	H(4)—H(5)		bay	5	√			
	3-Acetyl-9-Bromo	H(4)—H(5)		bay	5	√			
		H(4)—H(10)		epi	5	√			
	2,7-Dimethyl								CH_3—H(4)
	3,6-Dimethyl								CH_3—H(1)
	9-Methyl								CH_3—H(10)
	9-Fluoro	F—H(8)	0·5	peri F—H	4	√	√		
		F—H(5)	2·0	epi F—H	5	√	√		
	9,10 $(OR)_3$ 			none					
	9,10-Dihydro								CH_2-ring
	9-Formyl								H(9)—CHO
Triphenylene	Parent	H(1)—H(12)		bay	5	*			
	2-Methyl								CH_3—H(3) CH_3—H(4)
	1,3-Dimethyl								CH_3—H^{ortho}
	2,3-Dimethyl	H(1)—H(12)	0·45	bay	5			√	CH_3—H(1)
	2,7-Dimethyl	H(1)—H(12)		bay	5				CH_3—H(3)
	1,6,11-Trimethyl								CH_3—H(2) CH_3—H(8) CH_3—H(9) CH_3—H(4)
	2,6,11-Trimethyl								CH_3—H^{ortho}
	1,3,6,11-Tetramethyl								CH_3—H^{ortho}
	2,3,6,11-Tetramethyl	H(1)—H(12)	0·4	bay	5			√	CH_3—H(7) CH_3—H(8)
	2,3-Dimethoxy	H(1)—H(12)	0·4	bay	5			√	
	2-Methoxy-6,11-dimethyl								CH_3—H(7) CH_3—H(8) CH_3—H(9)
Benz[*a*]anthracene	Parent	H(1)—H(5)	0·4	epi	5	√	√		
		H(1)—H(12)		bay	5	√			
		H(6)—H(12)		epi	5	√			
		H(7)—H(11)		epi	5	√			
		H(8)—H(12)	0·3	epi	5	√	√		
		H(11)—H(12)		peri	4	√			
	7-Methyl								CH_3—H(12)
	7,12-Dimethyl								
Pyrene	Parent			none					
	1-Methyl								CH_3—H(2)
Benzo[*c*]phenanthrene	Parent	H(1)—H(5)	0·4	epi	5	√*		√	
		H(1)—H(8)	0·4		7	√		√	
Dibenzo[*c,g*,]phenanthrene	Parent	H(1)—H(5) or H(1)—H(6)	0·6	epi	5	√*		√	
Benzo[*k*]fluoranthene	Parent	H(1)—H(12)	0·25	bay	5	√		√	
		H(7)—H(11)	0·25	epi	5	√		√	
		or H(11)—H(12)		peri	4				
Fluorene	Parent			none					CH_2—H(1)
									CH_2—H(2)—H(3)
(Benzene)	*p*-Methylbenzylbromide								CH_2—H(2) CH_3—H(3)

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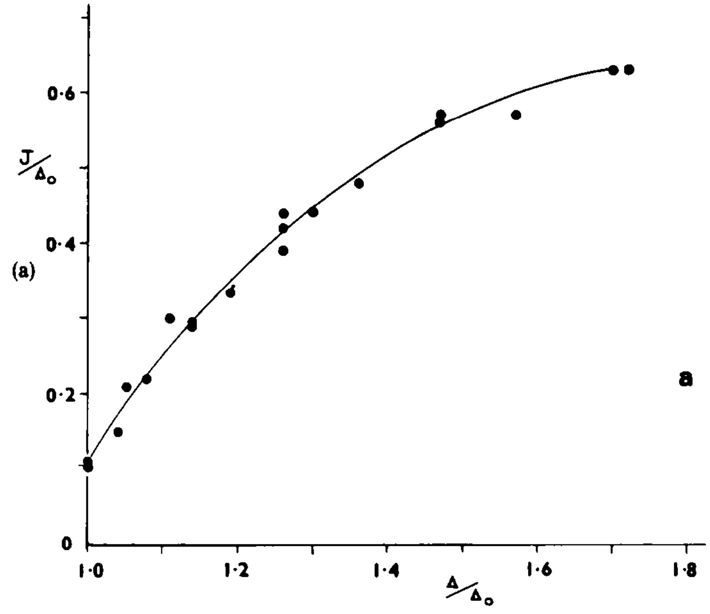
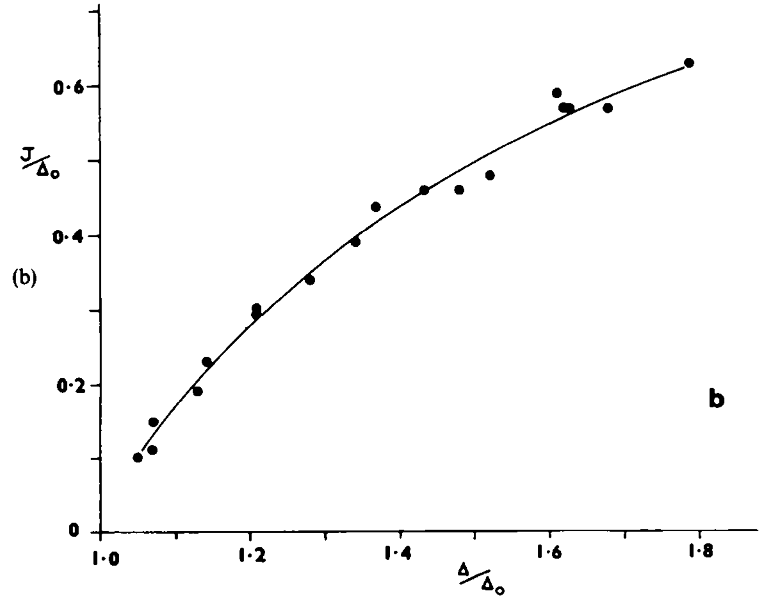
* Variable temperature measurements confirm that broadening does not arise from intramolecular relaxation.

POLYNUCLEAR HYDROCARBONS

Benzylic coupling						Other long-range coupling						
Magnitude (c/s)	Type	Bonds	Confirmed by DR	Measurement		Identity	Magnitude (c/s)	Type	Bonds	Confirmed by DR	Measurement	
				Direct	Indirect						Direct	Indirect
0·75	*para*	6	✓	✓								
	meta	5	✓									
0·2	*meta*	5	✓		✓							
1·1	*ortho*	4	✓	✓								
	ortho	4										
	meta	5	✓									
	para	6										
zero	Aldehydic											
0·5	*ortho*	4	✓		✓							
	meta	5	✓									
	ortho	4	✓									
	ortho	4	✓									
0·5	*ortho*	4	✓		✓							
0·5	*ortho*	4	✓		✓							
	meta	5	✓									
	meta	5	✓									
	para	6	✓									
	ortho	4	✓									
	ortho	4	✓		✓							
0·5	*ortho*	4	✓									
	meta	5	✓									
						OCH_3—H(1)	0·3	*ortho*	5	✓		✓
0·45	*ortho*	4	✓		✓	OCH_3—H(1)		*ortho*	5	✓		
	meta	5	✓									
	meta	5	✓									
0·7	*para*	6	✓	✓								
						CH_3—CH_3	0·55		7	✓		✓
0·6	*ortho*	4	✓		✓							
0·95	*ortho*	4										
0·4	*meta*	5										
	meta	5										
	para	6										
0·3	*ortho*	4				CH_2—CH_3	0·4		7	✓		✓
0·4	*ortho*	4										

and phenanthrene-9,10-quinone, has been reported, the H^1 spectrum does not appear to have been investigated. For a ~10% solution in $CDCl_3$, we find the doublet $C\underline{H}_3$ signal centred at $\delta = 3{\cdot}80$ ppm with $J = 13{\cdot}5$ c/s (c.f. 13 c/s and 13·5 c/s, respectively, in the adducts of trimethyl phosphite with phenylglyoxal and pyrene-4,5,9,10-diquinone[63]); the aromatic region shows the ABMX spectrum of a typical 9,10-disubstituted phenanthrene[4,5] with $|\delta_2 - \delta_3| \simeq 4$ c/s. The H(2,3) signals are





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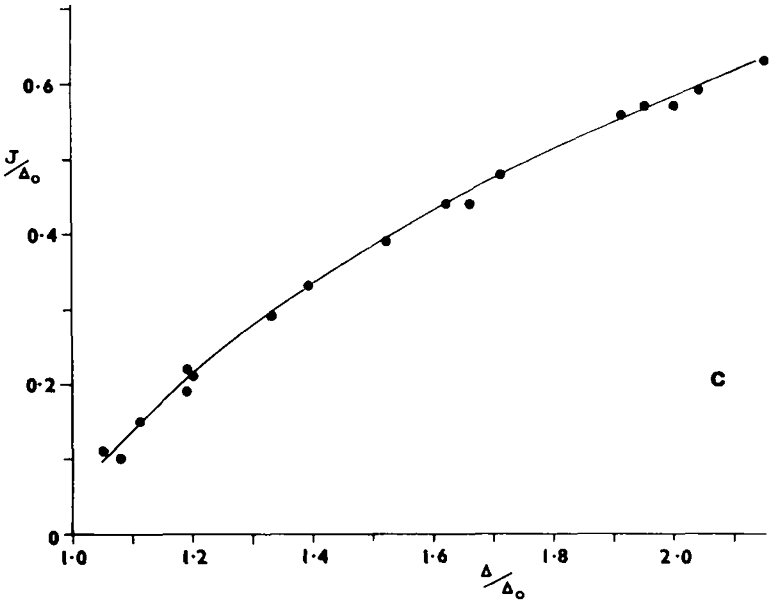

FIG. 1. Graphs of separation/single-line width ratio, J/Δ_0, vs. unresolved width/single-line width ratio, Δ/Δ_0, measured from computed spectra, for (a) doublets; (b) 1.2.1 triplets; and (c) 1.3.3.1. quartets.

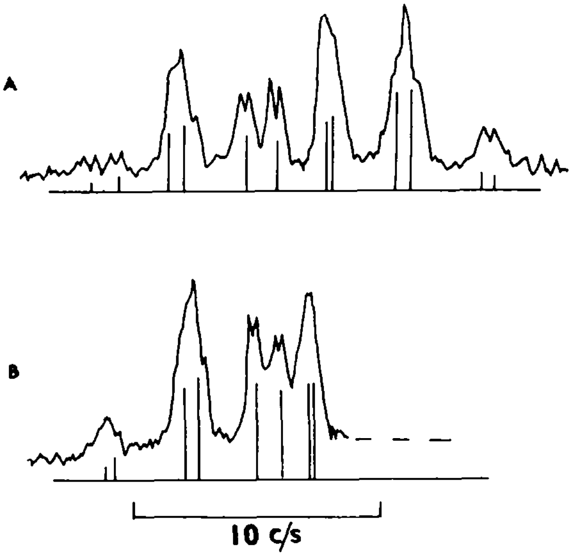

FIG. 2. Extra splittings arising from H(4) . . . H(5) coupling in 60 Mc/s H(4,5) spectra of, A, 9,10-diethyl- and, B, 9,10-dibromophenanthrenes. In each, the upper trace is the observed spectrum, while the stick plots represent spectra computed with no allowance for inter-ring coupling.

centred at $\delta = 7{\cdot}55$ ppm, those of H(1) and H(4) at $\delta = 8{\cdot}10$ ppm and 8·64 ppm respectively. Hamilton *et al.* have reported[64] the general form of the H^1 spectrum of the corresponding triisopropoxy derivative[62] (XI: R = iPr); in the aromatic region we again find an ABMX system, with H(2,3) at 7·54 ppm, H(1) at 8·07 ppm and H(4) at 8·64 ppm for a ~10% solution in $CDCl_3$. For both trimethoxy and triisopropoxy derivatives, the H(4) group shows no sign of extra multiplicity attributable to long-range coupling to the phosphorus atom. On the other hand, the F^{19} spectrum of 9-fluorophenanthrene[5] reveals a 2·0 c/s coupling, in addition to $J_{F-H(10)}$. The H^1 spectrum recorded during irradiation at the F^{19} frequency* confirmed that the smaller H–F splitting is attributable to $J_{F-H(5)}$, and also showed a third long-range coupling to fluorine. In the F^{19}-decoupled spectrum, the lowest-field components of the H(4), H(5) group are simplified; they now have apparent triplet form because of similar values of *para* H–H, and bay [H(4)–(5)] couplings. On the other hand, the higher field lines in this group show greater multiplicity and there is apparent a further long-range H–H coupling, presumably to H(10), (which has broad signals). These observations lead us to conclude that $\delta_4 < \delta_5$ in 9-fluorophenanthrene and to assign the $J = 2{\cdot}0$ c/s H–F coupling as between fluorine and H(5). In the reverse heteronuclear double-resonance experiment, irradiation at the frequency of the H(4), H(5) group caused the 2·0 c/s splitting in the F^{19} spectrum to collapse. The normal H^1 spectrum shows $J_{F-H(8)} = 0{\cdot}5$ c/s, since such splittings in the H(8) group are erased on irradiation at the F^{19} frequency.

In contrast with the multiplet structure of the methylene resonances of 4,5-methylenephenanthrene,[4] acenaphthene (X),[50] and fluorene,[6] the $C\underline{H}_2$ signal in the spectrum of 9,10-dihydrophenanthrene is singlet, with $\Delta = 1{\cdot}1 \pm 0{\cdot}05$ c/s in CCl_4 solution (c.f. 1·5 c/s in ref. 65). The narrowness of the signal is indicative of rapid conformational interconversion; this renders the two methylene protons equivalent on the time average,[65] even though U.V. evidence[66,67] and calculations from models[65,68,69] indicate that the aromatic rings are inclined at between 15 and 20° to each other. Further, benzylic couplings are evidently weaker than in 4,5-methylenephenanthrene. The aromatic region of the spectrum can be approximated as ABCX—the H(4,5) or X signals are shifted to low-field (7·66 ppm at infinite dilution in CCl_4) of the collapsed H(1–3) resonances ($\delta = 7{\cdot}03$–$7{\cdot}30$ ppm), and $J_{14} + J_{24} + J_{34} = 10{\cdot}2$ c/s (c.f. 10·3 in phenanthrene[4])—and both field (60 Mc/s) and frequency-sweep (100 Mc/s) double-resonance at $C\underline{H}_2$ brings about here only a slight and general narrowing.

Triphenylene and its derivatives

The origin of the broadening of bay-proton resonances in triphenylene[3] cannot be studied directly by double-resonance. As with phenanthrene, however, we detected no change in the width of these lines in spectra recorded at different temperatures (30, 60 and 90° in dioxan solution). Furthermore, in 2,3-dimethyl-, 2,3-dimethoxy-, and 2,3,6,11-tetramethyl-triphenylenes frequency sweep double irradiation at 100 Mc/s† confirmed that unresolved coupling to H(1) and H(4) remained after decoupling of the methyl or methoxy protons. Line-widths measured from those

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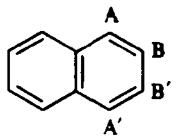
* We are grateful to Mr J. A. Deagan of Brücker Spectrospin Ltd for the 90 Mc/s heteronuclear decoupling experiments.

† We are indebted to Dr J. J. R. Reed and Mr T. Hines of ESSO Research and Development Division, and Dr D. Shaw of Varian Associates Ltd., for 100 Mc/s decoupling.



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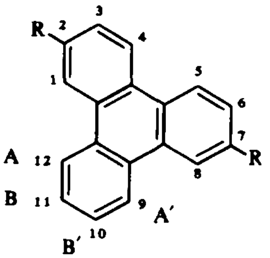

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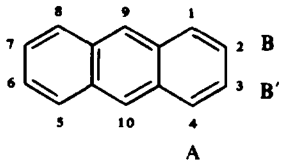

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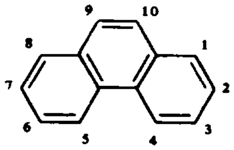

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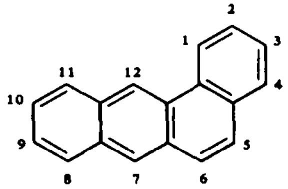

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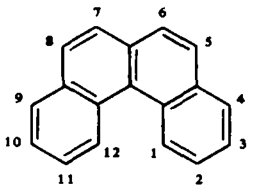

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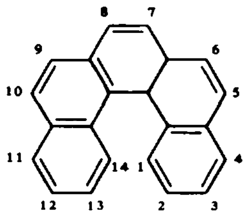

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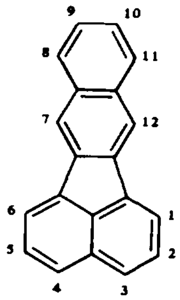
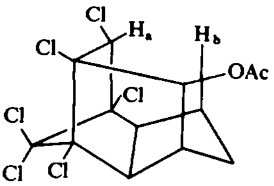
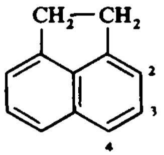


VIII



IX



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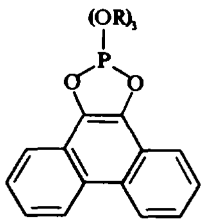

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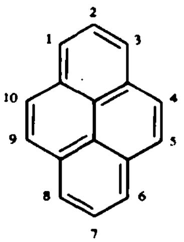

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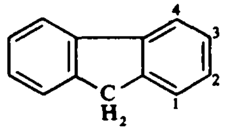


XIV

decoupled spectra correspond to $J_{1,12} = 0{\cdot}45$ c/s in the 2,3-dimethyl compound, and 0·4 c/s in both others. In all the mono-, di-, tri- and tetramethyltriphenylenes we have investigated, the expected *ortho* benzylic couplings are confirmed by spin decoupling; via Fig. 1(c) we were able to measure benzylic couplings indirectly in five compounds (Table 1). Spin decoupling also reveals small *meta* aromatic-to-methyl couplings in the 2-methyl-, 1,6,11-trimethyl, 2,3,6,11-tetramethyl, and 6,11-dimethyl -2-methoxy derivatives. A small coupling between methoxyl and *ortho* aromatic protons is evident in both 2,3-dimethoxy-, and 6,11-dimethyl-2-methoxy triphenylenes. With the assumption of negligible coupling between methoxyl protons and *meta* aromatic protons, we find $J_{\mathrm{OCH_3-H(1)}} = 0{\cdot}3$ c/s in the former.

Benz[a]*anthracene and its derivatives*

Partial assignments of the spectrum of benz[*a*]anthracene have been reported by several authors at 40[70], 60[22–24] and 100 Mc/s;[19] Batterham *et al.*[18] gave an approximate analysis of the complete 100 Mc/s spectrum in $CDCl_3$ solution. Our spin-decoupling experiments required assignment of a rather better-resolved 60 Mc/s spectrum than that previously reported.[18, 22] On the basis of 100 Mc/s and 220 Mc/s[71] spectra in CS_2 and Batterham's chemical shifts,[18] the peaks in the 60 Mc/s spectrum, as illustrated in Fig. 3, were assigned. Field-sweep double-irradiation allowed identification of the following couplings: epi long-range couplings between H(1) and H(5), H(6) and H(12), H(7) and H(11), and H(8) and H(12); peri coupling between H(11) and H(12); and a coupling between the bay protons H(1) and H(12). From a small splitting of the highest field H(5) line in the 100 Mc/s spectrum, we measured $J_{1,5}$ as 0·4 c/s, while small splittings of the H(8) multiplet indicated $J_{8,12} = 0{\cdot}3$ c/s.

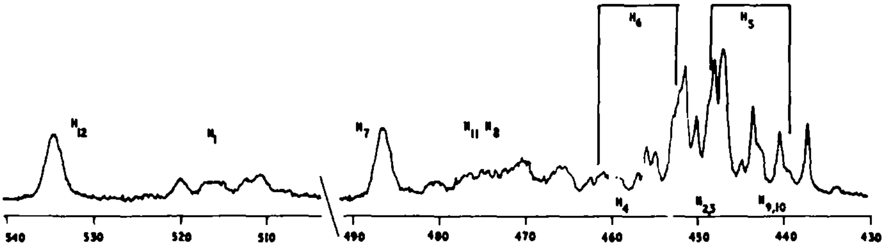
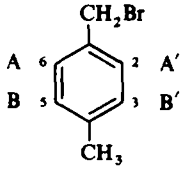


FIG. 3. 60 Mc/s spectrum of benz[*a*]anthracene in CS_2 solution.

We find a 0·7 c/s doublet for the methyl resonance of 7-methylbenz[*a*]anthracene; spin-decoupling shows this to arise from coupling to the *para* H(12). Double-irradiation also confirms a coupling between the *para* methyl groups in 7,12-dimethyl benz[*a*]anthracene; each methyl signal narrowed from $\Delta = 1{\cdot}85$ c/s when the other methyl frequency was irradiated. From Fig. 1 we estimate $J_{\mathrm{CH_3-CH_3}}$ as 0·55 c/s. The known deviation of the carbon of the 12-methyl group from the mean molecular plane in the 7,12-dimethylbenz[*a*]anthracene crystal[72] led us to suspect that the seven-bond methyl-methyl coupling is stereospecific; however, we have also been able to demonstrate a similar coupling between methyl and methylene protons in the unhindered *p*-methyl-benzylbromide (XII).

The 60 Mc/s aromatic AA'BB' system, decoupled from $C\underline{H}_2Br$ and $C\underline{H}_3$, was solved for an 11% w/w solution in CS_2 by the direct method of Dischler,[73–75] to give the



XII

$\nu_A = 427{\cdot}3$ c/s
$\nu_B = 420{\cdot}1$ c/s
$J_{AB} = 7{\cdot}95$ c/s, $J_{AB'} = 0{\cdot}55$ c/s
$J_{AA'} = 1{\cdot}9$ c/s, $J_{BB'} = 1{\cdot}9$ c/s

above parameters. Assuming negligible *meta* benzylic coupling, and regarding the *ortho* benzylic couplings as first-order perturbations, we found that a Lorentzian envelope computed with $J_{C\underline{H}_3Br-A} = 0{\cdot}3$ c/s, and $J_{CH_3-B} = 0{\cdot}4$ c/s fitted the undecoupled spectrum well. The CH$_2$ resonance was observed to sharpen both when decoupled from the A protons, and also when the CH$_3$ frequency was irradiated. The C$\underline{H}_3$—C$\underline{H}_2$Br coupling was estimated to be 0·4 c/s from the line-widths after decoupling from the aromatic protons. Furthermore, when the C$\underline{H}_2$Br frequency was irradiated, the CH$_3$ signal collapsed to a 0·4 cps triplet, in confirmation of the above value of J_{CH_3-B}.

Pyrene and 1-*methylpyrene*

The spectrum of pyrene (XIII) in CCl$_4$ (ref. 16 and our work) shows no sign of inter-ring coupling between the AB$_2$ H(1–3) and A$_2$ H(4,5) spin systems; resonances of all three proton types have Δ similar to that of TMS.

Clar *et al.* reported[52] J_{CH_3-H} ortho for a number of methylpyrenes. We have confirmed their observation of a methyl singlet for 1-methyl pyrene and, further, estimate the benzylic coupling as 0·6 c/s from measurement of the line-width of the H(2) resonances. Double-irradiation at the C$\underline{H}_3$ frequency confirmed that the highest-field aromatic signals were the H(2) lines of the H(2,3) AB system.

Benzo[c]*phenanthrene*

The broad H(1,12) resonances in the spectrum of benzo[*c*]phenanthrene showed neither detectable increase in Δ between +30° and −53° (four temperatures) in acetone solution, or between +32 and −62 in CS$_2$ (four temperatures), nor diminution between +14 and +69 (six temperatures) in benzene-d_6.[10] Thus a relaxation effect does not seem responsible for the line broadening, and unresolved inter-ring coupling was confirmed by field-sweep double-irradiation: sharpening of the highest-field H(5) line, such that it reaches the same height as its H(6) partner, was achieved in benzene-d_6 by irradiation at the H(1) frequency.[10] By regarding inter-ring coupling as a first-order perturbation[76] of the ABCD and AB systems, we made estimates from CS$_2$, acetone and benzene-d_6 solutions by comparing experimental (undecoupled) traces of the H(1) and H(5,6) regions with theoretical Lorentzian envelopes; close agreement was obtained for $J_{1,4} = J_{1,8} = 0{\cdot}4$ c/s.[10]

Dibenzo[c,g]*phenanthrene*

The lowest field signals of the dibenzo[*c,g*]phenanthrene spectrum (Fig. 4) assigned to H(1,14),[24] comprise a pair of poorly resolved doublets which neither broaden nor sharpen as the temperature is changed between −65 and +30° (four temperatures) in CS$_2$, and +30 and +72° (three temperatures) in benzene-d_6. In CS$_2$ solution, double irradiation sharpened the H(1,14) signals. The necessary frequency differences

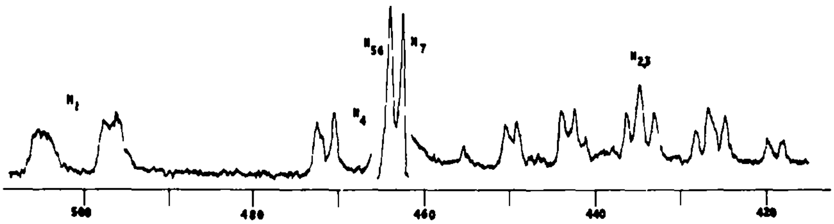


FIG. 4. 60 Mc/s spectrum of dibenzo[*c,g*]phenanthrene in CS_2 solution.

corresponded to the lower-field (broad) component of the intense doublet near 464 c/s. In benzene-d_6 solution, the latter broad signal separated further into a sharp high-field line superposed on a broader partner; these two were assigned to the inner lines of the H(5,6) AB system, as in benzo[*c*]phenanthrene. By causing the broad H(5,6) line to sharpen, field-sweep double-resonance with irradiation of H(1,14) confirmed long-range coupling to H(1); by comparison of computed and experimental envelopes, its magnitude was estimated as 0·6 c/s.

Benzo[k]*fluoranthene*

In a previous paper,[7] we reported how both field- (60 Mc/s) and frequency-sweep (100 Mc/s) double-irradiation confirmed H(1)–H(12) coupling as well as the anticipated H(7)–H(11) epi or H(11)–H(12) peri coupling. Measurement of Δ of normal and decoupled H(12) signals at 100 Mc/s and use of Figure 1 leads to $J = 0{\cdot}25$ c/s for both couplings.

Fluorene (XIV)

The breadth of the signal from the $C\underline{H}_2$ group ($\Delta = 2{\cdot}5$ c/s at both 60 and 100 Mc/s) suggests that these protons are coupled to the aromatic rings. Confirmation of this benzylic coupling comes from the sharpening of peaks and reduction in multiplicity which occurs throughout the aromatic spectrum which results from field- (60 Mc/s) and frequency-sweep (100 Mc/s, irradiation at the $C\underline{H}_2$ frequency. Analyses of the 60 and 100 Mc/s decoupled spectra have been published.[6] Comparison of the normal and decoupled spectra shows that the H(1) signals are split into 0·95 c/s triplets; the H(4) signals are broadened by an amount which, according to Fig. 1(b), corresponds to $J_{CH_2-H(4)} = 0{\cdot}4$ c/s. The H(2,3) multiplet is also long-range coupled to $C\underline{H}_2$; lines characteristic of both H(2) (*meta*), and H(3) (*para*) are broadened. After decoupling from $C\underline{H}_2$, the H(4) lines had Δ close to that of TMS. No H(4)–H(5) inter-ring coupling was detected in fluorene.

Measurements of long-range coupling constants on all the hydrocarbons and their derivatives are summarised in Table 1. In this, inter-ring couplings are further classified as bay, epi, or peri, and benzylic couplings as ortho, meta, para, or aldehydic.

EXPERIMENTAL

Solvents were acetone and carbon tetrachloride (both BDH "Analar" grade), carbon disulphide (BDH laboratory reagent "for IR spectroscopy"), and benzene-d_6 (Ciba, isotopic purity >99 atom %D); all contained a little tetramethylsilane (TMS) as internal reference (Aldrich Chemical Co. Inc.). Improved resolution was obtained in some cases by either passing through nitrogen or shaking with a 10% sodium dithionite solution.[34]

60 Mc/s spectra were recorded on a Varian A-60 with a V-6058A (field-sweep) spin decoupler and a V-6057 variable-temperature system. Sweep widths were calibrated vs. the separation between 2% benzene, 2% TMS in CCl_4. The latter separations and the double-resonance frequency differences were checked against an Advance TC2 timer/counter. Probe temperatures were measured by recording spectra of methanol (below room temperature) and ethylene glycol (above).[55] 100 Mc/s spectra were recorded on Varian HA-100 spectrometers.

Computations were carried out on the Bradford University ICT 1909 computer, and theoretical spectra were plotted on a Benson Lehner XY recorder fed by the Bradford University Stantec Zebra.

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