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IDENTIFICATION OF AN ETHYL-9,10-DIMETHYLPHENANTHRENE BY HIGH-RESOLUTION NUCLEAR MAGNETIC RESONANCE

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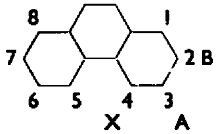
Abstract—The position of substitution of an ethyl-9,10-dimethylphenanthrene has been deduced from NMR studies at 60 Mc/s of the aromatic protons. The method used was to compare the spectra of the ethyl derivative, and the acetyl compound from which it was prepared, with those of alkylphenanthrenes of known structure. The spectra have been analysed as ABX and ABMX spin systems.

ALTHOUGH high resolution NMR has been used to determine the position of substitution in many methyl-substituted polycyclic hydrocarbons,[1–4] hitherto the method has been to compare the chemical shift differences between methyl groups in different positions. In this paper, we show that the same kind of prediction can be made for an ethyl substituted 9,10-dimethylphenanthrene by a study of the *aromatic* part of the spectrum at a frequency of 60 Mc/s.

The unknown compound was obtained by reduction of an acetyl-9,10-dimethylphenanthrene. The acetylation of 9,10-dimethylphenanthrene was investigated[5] in the expectation that this system would be more amenable than phenanthrene to an examination of the postulated[6] interconversion of 2- and 3-acetylphenanthrene. Only one acetyl derivative was isolated, and this was tentatively identified as 3-acetyl-9,10-dimethylphenanthrene on the basis of the behaviour of the derived amine.

The basis of the NMR method is the solution of the spectrum of phenanthrene given by Batterham *et al.*[7] They assumed, as in previous work,[8] that there are significant low-field steric shifts for the 1,4 protons, and so derived starting parameters by treating the system as ABMX (as in the diagram);



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[4] P. Durand, J. Parello, N. P. Buu-Hoi and L. Alais, *Bull. Soc. Chim. Fr.* 2438 (1963).

[5] P. M. G. Bavin, *Canad. J. Chem.* **38**, 911 (1960).

[6] P. H. Gore, *Chem. Rev.* **55**, 229 (1955).

[7] T. J. Batterham, L. Tsai and H. Ziffer, *Austral. J. Chem.* **17**, 163 (1964).

[8] N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.* **36**, 2443 (1962).

these were then refined in a symmetrical ABCD system (viz. with $J_{12} = J_{34}$, $J_{13} = J_{24}$) by an iterative computer method. We have also studied the spectrum of 9,10-dimethylphenanthrene in a similar way; the signals from H_1 and H_8 now appear almost midway between those of H_2, H_3 (and H_6, H_7) and H_4, H_5 (Fig. 1), instead of close to

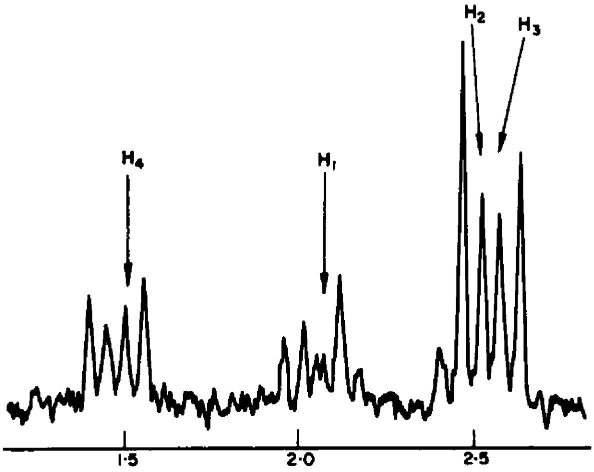

Fig. 1. 9,10-dimethylphenanthrene.

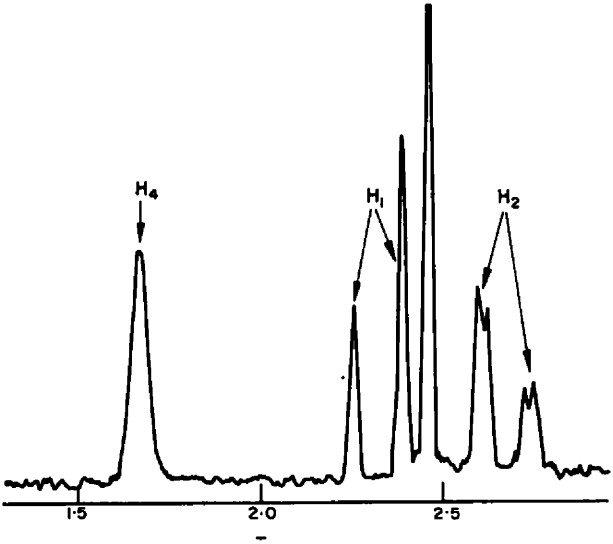

Fig. 2. 3,6-dimethylphenanthrene.

H_2, H_3 as in phenanthrene. With this assignment, the spectrum can be analysed as an ABMX system to give a calculated spectrum which fits the experimental line positions well, but shows a distortion of the intensities within the AB, M, and X groups. The parameters were then refined by treating the spectrum as a symmetrical ABCD system.* The two sets of data, ABMX and refined ABCD, compared sufficiently well to

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suggest that the more approximate ABMX parameters can be used in making positional assignments. The effect of alkyl substituents at other positions has also been

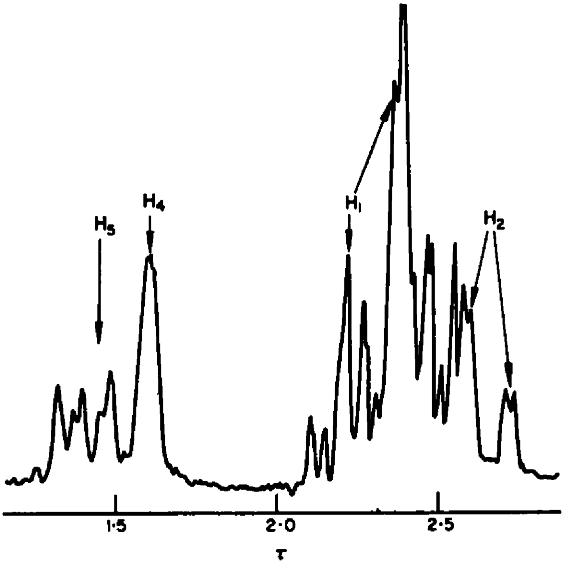

FIG. 3. 3-methylphenanthrene.

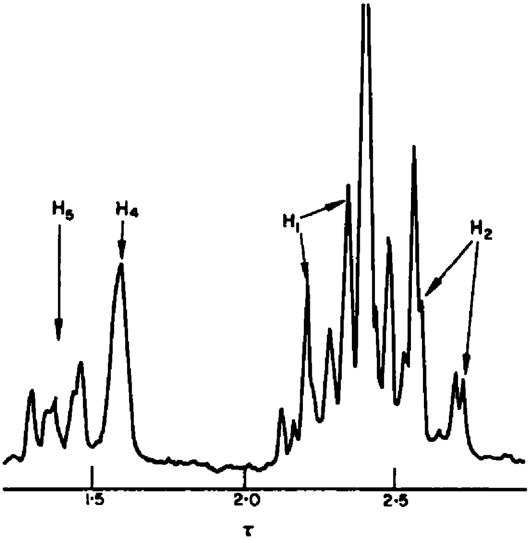

FIG. 4. 3-ethylphenanthrene.

studied and the analyses are summarized in Table 1. The spectrum of 3,6-dimethylphenanthrene (Fig. 2) is solved by an ABX treatment ($A = H_1$, $B = H_2$, $X = H_4$) almost exactly, since $\nu_X - \nu_B/J_{BX}$ is about 30. In the spectra of 3-methyl- and 3-ethylphenanthrene (Figs. 3 and 4), the resonances of H_2 and H_4 in the substituted ring are shifted to a slightly higher field than those of H_7 and H_5 respectively in the unsubstituted ring. The H_4 signal takes the form of a broad singlet (width ~5 c/s), presumably because of weak and unresolved coupling to H_1 and H_2. Thus the ABX system H_1, H_2 and H_4 may be distinguished from H_5, H_6, H_7 and H_8 and an analysis made.

The ethyl substituted 9,10-dimethylphenanthrene gave the spectrum reproduced in Fig. 5. By analogy with 9,10-dimethylphenanthrene, the lines of the ABMX pattern of H_5, H_6, H_7 and H_8 can be readily picked out, since the separation of the outermost strong lines of the AB, M, and X groups will be very nearly the same. As for the rest, the broad singlet 0·2 ppm to the high-field side of the centre of H_5 (X, at the lowest field) has an intensity equivalent to one proton, and is in the predicted position for H_4 with small *meta* and *para* couplings. On the high-field side of this, H_8 (M) is superimposed on two slightly broadened lines separated by 8·4 c/s, which we attribute to H_1 coupled to another proton with $J = 8{\cdot}4$ c/s. The magnitude of this coupling suggests that the latter must be an *ortho* proton; in confirmation, we find in the highest field group two doublets, whose centres are 8·4 c/s apart, which we assign as H_2 lines. We conclude that the spectrum is explained if the ethyl group is in the 3-position.

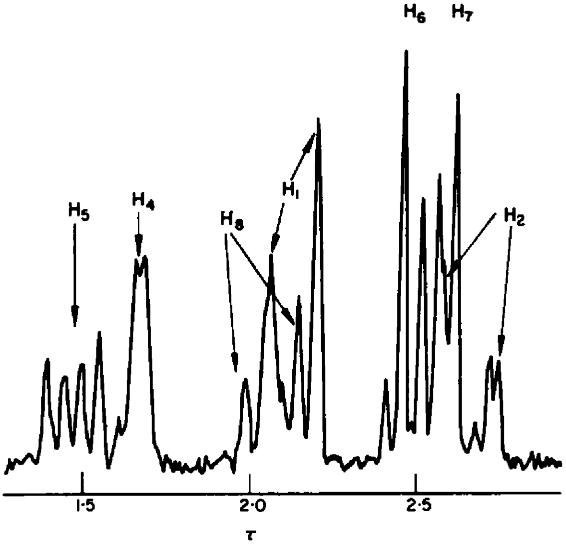

FIG. 5. Ethyl substituted 9,10-dimethylphenanthrene.

Further confirmation of this assignment comes from the ring spectrum (Fig. 6) of the acetyl compound from which the ethyl derivative was prepared by reduction. The ABMX pattern of H_5, H_6, H_7 and H_8 is again present, but now the broad H_4 resonance is shifted to the low-field side of H_5 through some effect characteristic of the acetyl group, as was noted by Martin *et al.*[9] in 3-acetylphenanthrene. For the same reason, H_2 moves downfield to a position near that of the H_1 (and H_8) signals. H_1 and H_2 again form the AB part of an ABX system, which we have not been able to assign at 60 Mc/s because of the similarity between the values of $\nu_A - \nu_B$ and J_{AB}. The chemical shifts and coupling constants derived from the spectra of both the 3-ethyl and 3-acetyl compounds are given in Table 1.

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[9] R. H. Martin, N. Defay, F. Geerts-Evrard and H. Figeys, *Bull. Soc. Chim. Belg.* 73, 199 (1964).

In final confirmation of these assignments, we may consider the spectra we would predict were substitution to have occurred in other positions. (i) In 4-ethyl-9,10-dimethylphenanthrene the signals at $\tau < 1{\cdot}8$ ppm would correspond to one proton (H$_5$)

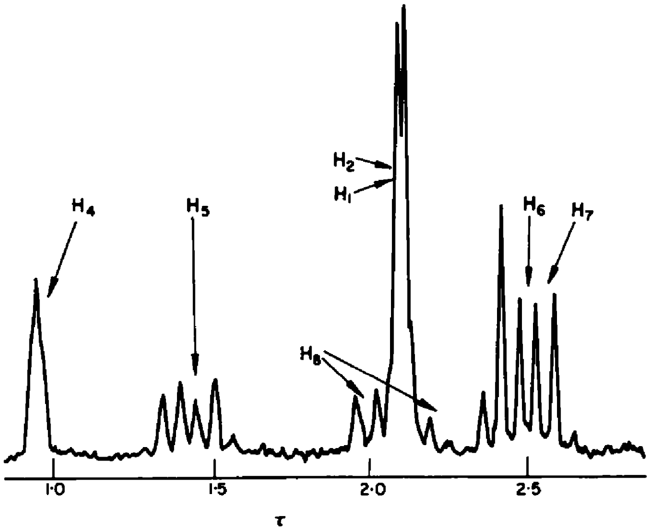

Fig. 6. 3-acetyl-9,10-dimethylphenanthrene.

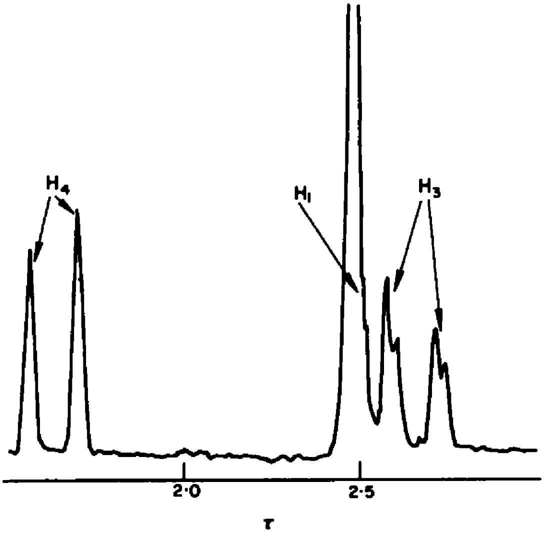

Fig. 7. 2,7-dimethylphenanthrene.

rather than two in the observed spectrum. Furthermore, we would expect an extra downfield shift of about 0·3 ppm, by analogy with the shift of 0·28 ppm observed both in this work and in Ref. 9 for H$_5$ of 4-methylphenanthrene relative to H$_4$, H$_5$ of phenanthrene. (ii) In 2-ethyl-9,10-dimethylphenanthrene we expect a reasonably sharp doublet for H$_4$ as in 2,7-dimethylphenanthrene (Fig. 7) rather than the broad singlet observed. Figure 7 also shows that H$_1$ would be expected to lie at a higher field than

TABLE 1. CHEMICAL SHIFTS AND COUPLING CONSTANTS IN PHENANTHRENE AND SUBSTITUTED PHENANTHRENES

Compound	Phenanthrene	9,10-dimethyl-phenanthrene	9,10-dimethyl-phenanthrene	3,6-dimethyl-phenanthrene	3-methyl-phenanthrene	3-ethyl-phenanthrene	3-ethyl-9,10-dimethyl-phenanthrene	3-acetyl-9,10-dimethyl-phenanthrene
Spin system solution and conc.	Symmetrical ABCD 10% in $CDCl_3$	ABMX I.D. in CS_2	Symmetrical ABCD I.D. in CS_2	ABX I.D. in CS_2	ABX I.D. in CCl_4	ABX I.D. in CCl_4	ABX'A'B'MX' I.D. in CS_2	ABMX I.D. in CS_2
ν_1	1·875	2·025	2·035	2·38	2·32	2·275	2·11	N.M.
ν_2	2·175	2·535	2·525	2·715	2·675	2·645	2·65	N.M.
ν_3	2·12	2·55	2·54	—	—	—	—	—
ν_4	1·07	1·45	1·455	1·685	1·61	1·58	1·665	0·91
ν_5	1·07	1·45	1·455	1·685	1·40	1·36	1·455	1·415
ν_6	2·12	2·55	2·54	—	N.M.	N.M.	2·54	2·49
ν_7	2·175	2·535	2·525	2·715	N.M.	N.M.	2·54	2·49
ν_8	1·875	2·025	2·035	2·38	N.M.	N.M.	2·04	2·02
J_{12}	8·4	9·0	8·5	8·2	8·2	8·0	8·4	N.M.
J_{13}	1·6	0·9	1·4	—	—	—	—	—
J_{14}	0·5	0·5	0·5	0·3	0·4	0·4	0·3	N.M.
J_{23}	7·3	6·9	6·9	—	—	—	—	—
J_{24}	1·6	1·7	1·4	1·8	1·6	1·6	1·8	N.M.
J_{34}	8·4	8·0	8·5	—	—	—	—	—
J_{56}	8·4	8·0	8·5	—	N.M.	N.M.	8·5	8·3
J_{57}	1·6	1·7	1·4	1·8	N.M.	N.M.	1·2	1·5
J_{58}	0·5	0·5	0·5	0·3	N.M.	N.M.	0·4	0·4
J_{67}	7·3	6·9	6·9	—	N.M.	N.M.	6.9	7·0
J_{68}	1·6	0·9	1·4	—	N.M.	N.M.	1·3	1·4
J_{78}	8·4	9·0	8·5	8·2	N.M.	N.M.	8·6	8·3

Chemical Shifts (ν) in p.p.m. on τ-scale. I.D. = Infinite dilution.
Coupling constants (J) in c/s. N.M. = Not measured.

H_8. (iii) Finally, in 1-ethyl-9,10-dimethylphenanthrene we expect the H_4 lines to consist of a complex pattern superimposed on H_5 and resonance from only one proton (H_8) would be found near $\tau = 2{\cdot}1$ ppm.

This method of study could be of use in the identification of alkyl phenanthrenes such as are obtained by the dehydrogenation of natural products.[10]

Acknowledgments—This work was supported in part by a grant from the Coal Tar Research Association. The NMR spectra were obtained on the Bradford Institute of Technology Varian A-60 spectrometer, by kind permission of Dr. E. G. Edwards, Dr. R. L. Elliott and Dr. D. W. Jones.

[10] A. J. Solo and S. W. Pelletier, *Analyt. Chem.* 35, 1584 (1963).