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APPLICATIONS OF NMR SPECTROSCOPY IN THE FIELD OF POLYCYCLIC AROMATIC COMPOUNDS—VIII

BIPHENYLENE AND BENZOBIPHENYLENE DERIVATIVES[1,2]

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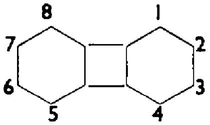
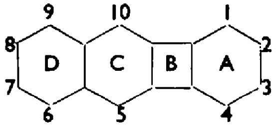
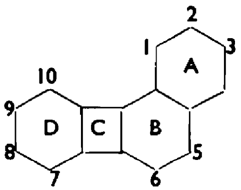
Abstract—NMR spectra of benzo [b] biphenylene and of substituted biphenylenes, benzo [a] biphenylenes and benzo [b] biphenylenes have been recorded at 60 Mc. These spectra fully confirm the structures previously assigned to the twelve derivatives examined in this work. The expected spectrum of benzo [a] biphenylene is deduced from the spectra of its substituted derivatives. The main results are summarized in Figs. 1 and 2.

Résumé—Les spectres RMN du benzo [b] biphénylène et de dérivés du biphénylène, du benzo [a] biphénylène et du benzo [b] biphénylène ont été relevés à 60 Mc. Ces spectres confirment les structures attribuées précédemment aux douze composés substitués repris dans ce travail. Le spectre présumé du benzo [a] biphénylène a été déduit de l'examen de ses dérivés substitués. Les résultats essentiels de ce travail sont rassemblés dans les Fig. 1 et 2.

IN THE preceding papers of this series, we have shown that NMR spectroscopy can be used to solve many problems in the field of substituted alternant polycyclic aromatic hydrocarbons. It was therefore of interest to extend our research to the biphenylene and benzobiphenylene series.







In 1958, Baker *et al.*[3] pointed out that three methods are generally used to determine the orientation of radicals introduced by direct substitution in the biphenylene nucleus:

(a) unambiguous synthesis starting from substituted biphenyls (e.g. 2-bromobiphenylene[3])
(b) degradation of the biphenylene derivatives to biphenyls of known structures, using Raney nickel (e.g. 2-acetylbiphenylene[4])

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[1] Part I: R. H. Martin, *Tetrahedron* **20**, 897 (1964).
[2] Part VII: R. H. Martin, N. Defay and F. Geerts-Evrard, *Tetrahedron* **20**, 1505 (1964).
[3] W. Baker, J. W. Barton and J. F. W. McOmie, *J. Chem. Soc.* 2658 (1958).
[4] W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.* 1476 (1954).

(c) interconversion of biphenylene derivatives (e.g. 2-acetylbiphenylene[4] → 2-aminobiphenylene ← 2-benzoylbiphenylene[5]).

These chemical proofs, although very convincing, are often time consuming for they generally involve laborious synthetic work, particularly when two or more substituents are present.

We have therefore examined the possibility of obtaining reliable information concerning the structures of substituted biphenylenes by NMR spectroscopy. In some cases, minor chemical transformations (such as an esterification) may nevertheless be necessary prior to the recording of spectra.

GENERAL DISCUSSION

The spectra recorded in this work are reported in the form of diagrams in Figs. 1 and 2.

DIAGRAMMATIC REPRESENTATION OF NMR SPECTRA[a] OF BIPHENYLENE DERIVATIVES: AROMATIC REGION

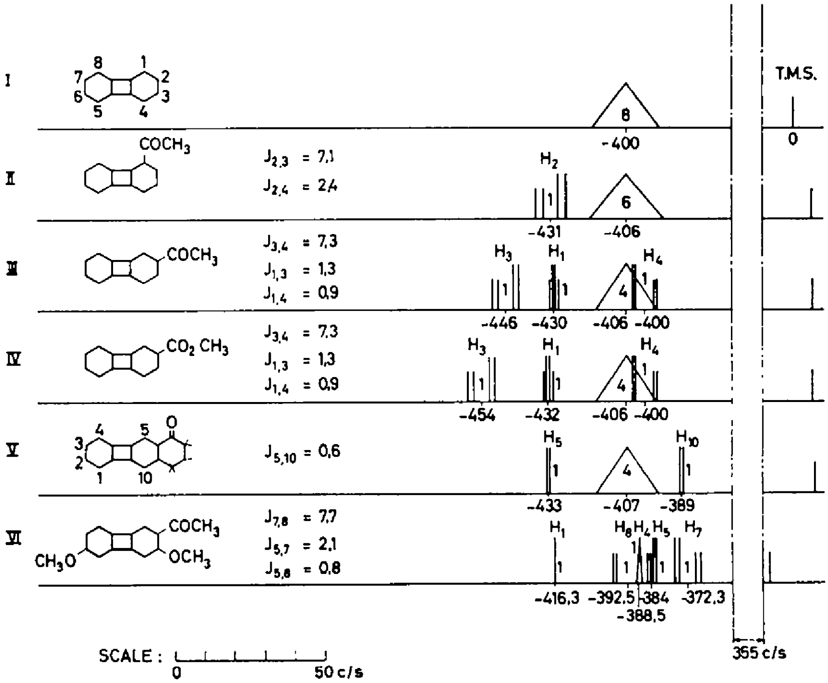

FIG. 1

[a] Chemical shifts are arbitrarily assigned to the center of the multiplets and expressed in c/s at 60 Mc. (internal reference: TMS = 0). The J values were simply measured on the spectra. In each series, the high field signals of the unperturbed protons are arbitrarily aligned with the signals of the corresponding protons in the unsubstituted hydrocarbons.

Chemical shifts of the aliphatic protons:
II $COCH_3$ (s) −148; III $COCH_3$ (s) −148; IV $COOCH_3$ (s) −230; V CH_2 position 7 (tr) −164, position 8 (q) −121, position 9 (tr) −153; VI $COCH_3$ (s) −150, OCH_3 (s) −231,5 and −223.

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[5] J. M. Blatchly, J. F. W. McOmie and S. D. Thatte, *J. Chem. Soc.* 5090 (1962).

DIAGRAMMATIC REPRESENTATION OF NMR SPECTRA[a] OF BENZOBIPHENYLENE DERIVATIVES: AROMATIC REGION

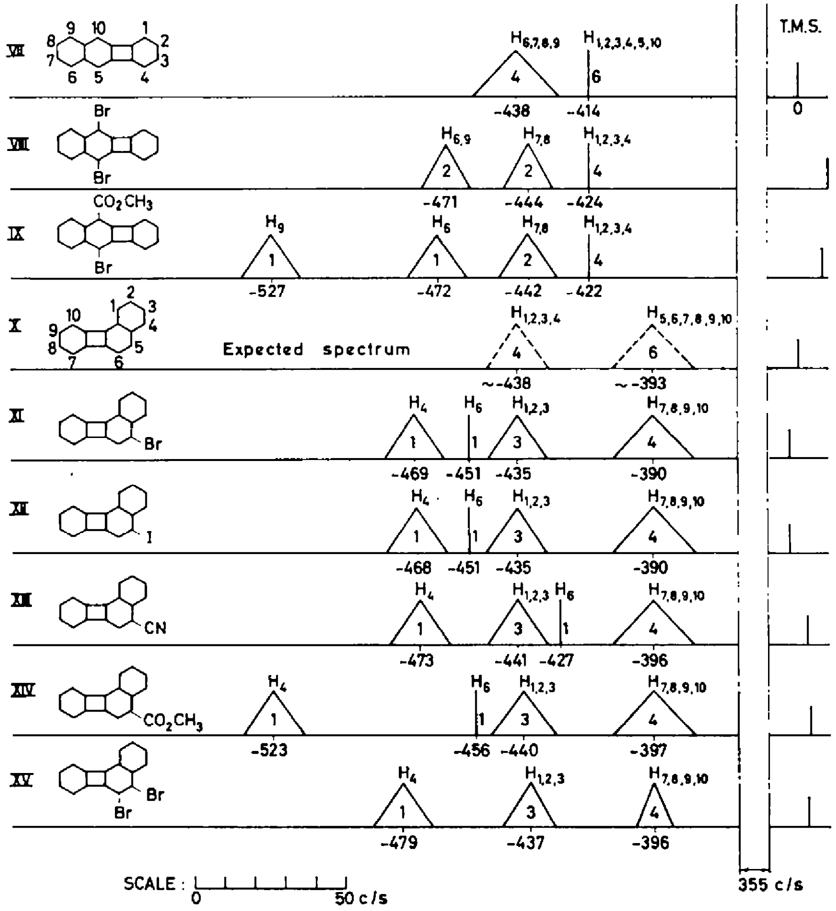

FIG. 2

[a] See footnote Fig. 1.

Chemical shifts of the aliphatic region: IX $COOCH_3$ (s) −236; XIV $COOCH_3$ (s) −236.

I. *Unsubstituted hydrocarbons*

The signals of the aromatic protons of biphenylene (400 c/s) and benzo [b] biphenylene (414 and 438 c/s) are at higher fields than those of the corresponding protons in purely benzenoid hydrocarbons (e.g. benzene 436 c/s, naphthalene 445 and 467 c/s).

From the study of substituted derivatives (*vide infra*), we have reached the conclusion that the protons of benzo [a] biphenylene must be very similar to those of benzo [b] biphenylene but with the six biphenylene protons ($H_{5,6,7,8,9,10}$) situated at a still higher field (~393 c/s instead of 414 c/s).

I.1 *Biphenylene* (I). The spectrum of biphenylene is that of an A_2B_2 system with $\delta_A - \delta_B = 6{,}24$ c/s.[6] In view of the fact that in naphthalene $\delta_A - \delta_B$ is much larger (= 20 c/s), no reliable analogy can be drawn between the two systems. The very small difference in chemical shift between the two types of protons seems to

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[6] G. Fraenkel, Y. Asahi, M. J. Mitchell and M. P. Cava, *Tetrahedron* **20**, 1179 (1964).

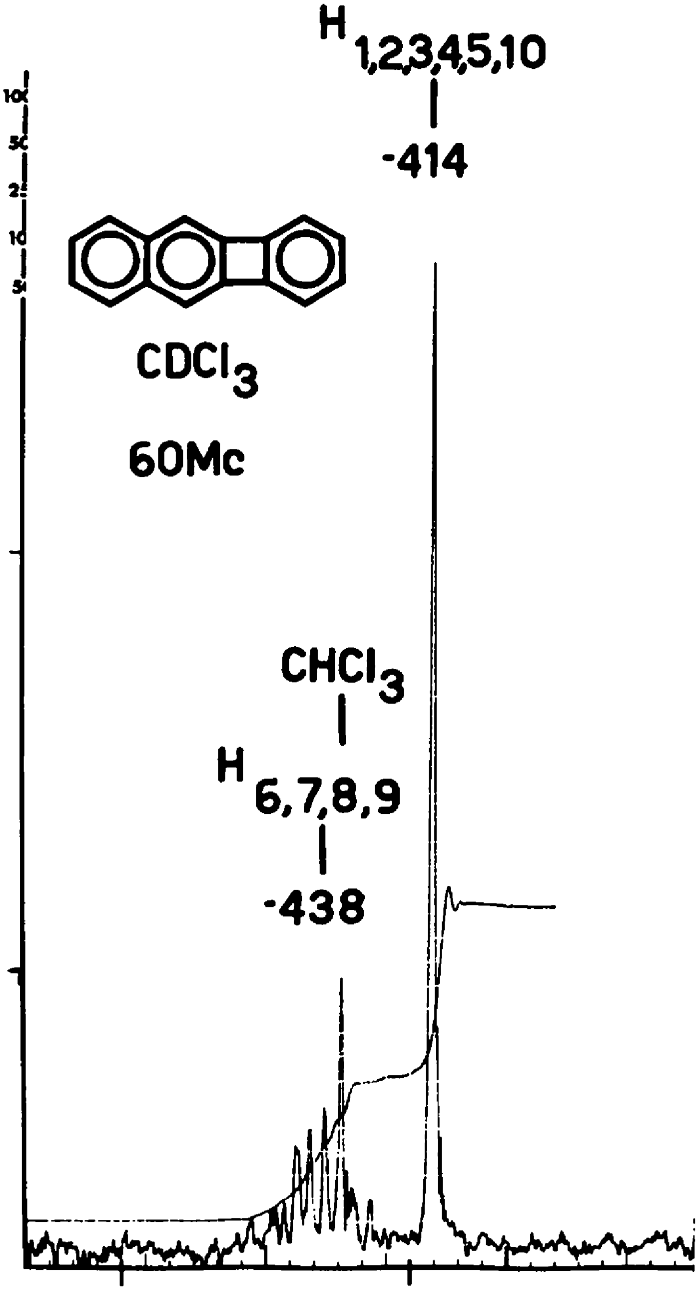
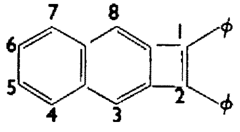


FIG. 3

imply that the α protons experience practically no *specific* influence from the central four-membered ring. It is therefore impossible to tell, *a priori*, which of the two sets of protons, α or β, appears at lower field.

I.2 *Benzo* [b] *biphenylene* (VII; Fig. 3). The spectrum of this hydrocarbon contains one broad singlet (6H) at 414 c/s and a multiplet (4H) centered at 438 c/s. From the study of the 5,10-disubstituted derivatives, it is clear that the low field protons are those of ring D ($H_{6,7,8,9}$) which belong to an A_2B_2 system. The six remaining protons from ring A and C are therefore equivalent. This assignment is further justified by a recent report of the spectrum of 1,2-diphenylnaphtho [b]-cyclobutadiene (XVI) by Cava *et al.*[7]



XVI

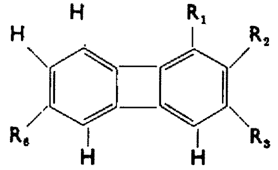
In this spectrum, two protons (H_3 and H_8) appear as a sharp singlet at 390 c/s, while the remaining 14 protons give rise to a multiplet in the "usual aromatic region".

I.3 *Benzo* [a] *Biphenylene* (X; Expected Spectrum). As already mentioned, it is almost certain, from the study of substituted derivatives, that the NMR spectrum of benzo [a] biphenylene will show two multiplets, one near 393 c/s containing the six protons of ring B and D, and one near 438 c/s containing the four protons of ring A.

It is important in this connection to note that in benzo [a] biphenylene H_1 and H_{10} are not comparable to the "angular protons" H_4 and H_5 (H-α3) of phenanthrene.

II. *Substituted derivatives*

TABLE 1. SHIELDING AND DESHIELDING EFFECTS[a] IN SUBSTITUTED BIPHENYLENES

			H_1	H_2	H_3	H_5	H_7
II	$R_1 = COCH_3$	$R_{2,3,6} = H$	—	−25 c/s	—	—	—
III	$R_2 = COCH_3$[b]	$R_{1,3,6} = H$	−24 c/s	—	−40 c/s	—	—
IV	$R_2 = COOCH_3$	$R_{1,3,6} = H$	−26 c/s	—	−48 c/s	—	—
V	$R_2 = CO—CH_2$ $R_3 = CH_2—CH_2$	$R_{1,6} = H$	−26 c/s (H_6)	—	—	—	—
VI	$R_2 = COCH_3$[c] $R_3 = OCH_3$ $R_6 = OCH_3$	$R_1 = H$	−24 c/s	—	—	+8·5 c/s	+20 c/s

[a] These values represent the difference in chemical shift between the perturbed protons and the multiplet containing the unperturbed protons of the same molecule (+shielding; −deshielding). In VI, H_8 was used as reference.

[b] See Fig. 4.

[c] See Fig. 5.

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[7] M. P. Cava, B. Hwang and J. P. Van Meter, *J. Amer. Chem. Soc.* **85**, 4032 (1963).

II.1 *Biphenylenes substituted at position* 1. In 1-acetylbiphenylene (II) only one proton (H_2) is deshielded (−25 c/s) by the substituent and this deshielding is practically of the same magnitude as that of H_1 in 2-acetylbiphenylene (−24 c/s; III).

We have already reported similar results in the phenanthrene series[8] (e.g. H_3 in 2-acetylphenanthrene: −29 c/s; H_2 in 3-acetylphenanthrene: −27 c/s).

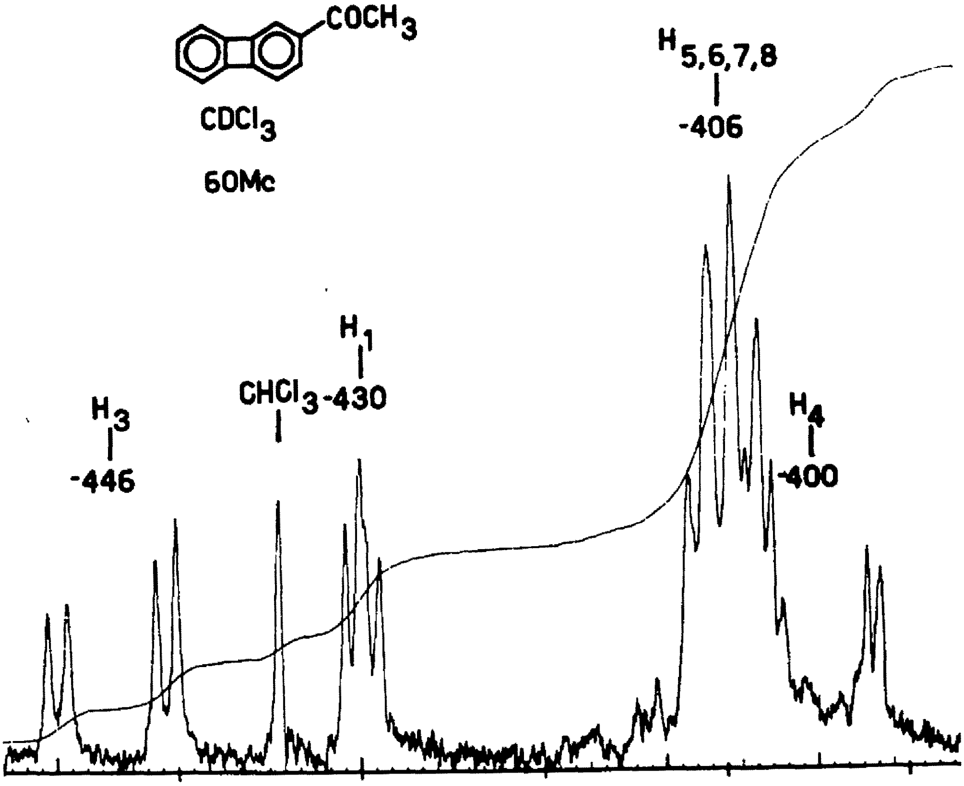

FIG. 4

II.2 *Biphenylenes substituted at position* 2. In the monosubstituted derivatives studied in this work, both *ortho* protons (H_1 and H_3) are deshielded and are clearly apparent in the spectra. Protons of the unsubstituted ring give rise to a multiplet having the same pattern as in biphenylene itself. From the results summarized in Table 1 it can be seen that the shielding and deshielding effects are much greater on the β protons than on the α protons. This observation is of interest in view of the fact that the reverse is true in the naphthalene,[9] the phenanthrene[8] and the triphenylene[10] series, although in these cases the differences are usually smaller.

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

[9] G. O. Dudek, *Spectrochim. Acta* **19**, 691 (1963).

[10] R. H. Martin, N. Defay and F. Geerts-Evrard, *Tetrahedron* **20**, 1091 (1964).

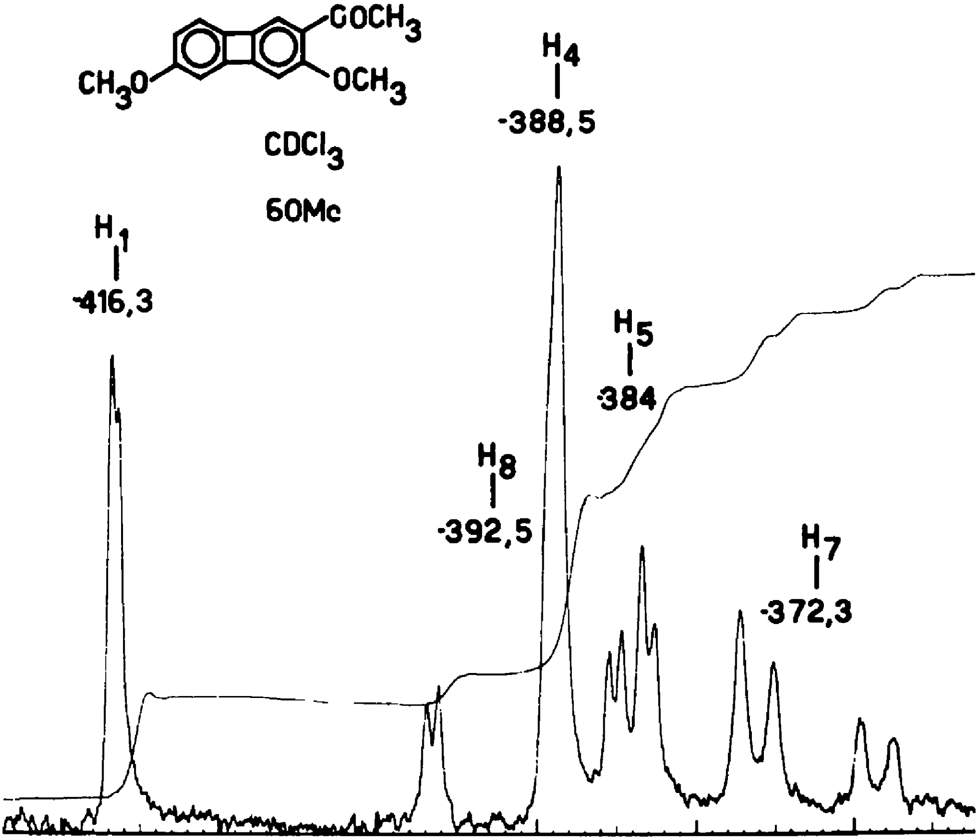
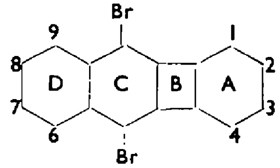
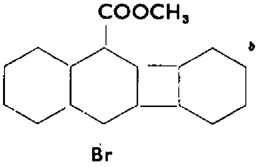


Fig. 5

Table 2. Deshielding effects[a] in disubstituted benzo [b] biphenylenes

		H_6	H_9
VIII		−19 c/s	−19 c/s
IX		−22 c/s	−77 c/s

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[a] These values represent the difference in chemical shift between the perturbed protons and the β protons of the same molecule, minus 8 c/s ($\delta_\alpha - \delta_\beta \sim 8$ c/s in the corresponding unsubstituted hydrocarbon).

[b] See Fig. 6.

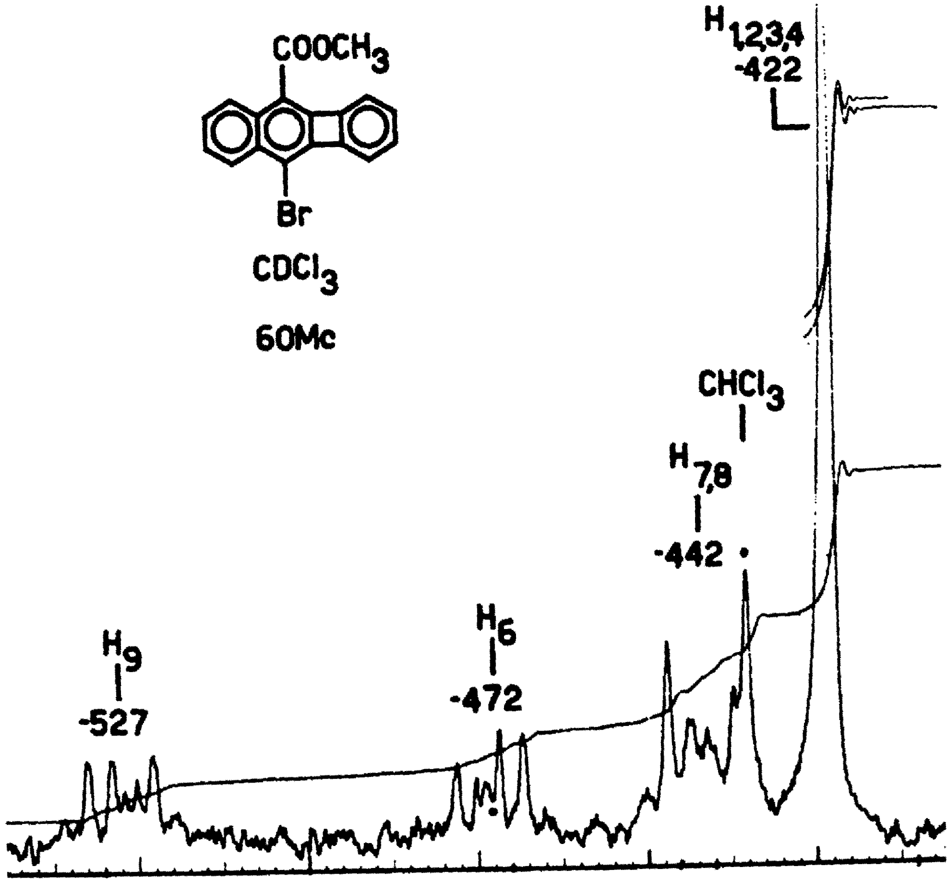
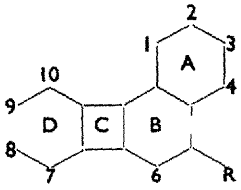
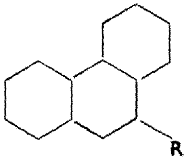


FIG. 6

TABLE 3. DESHIELDING EFFECTS IN SUBSTITUTED DERIVATIVES OF BENZO [a]-BIPHENYLENE AND PHENANTHRENE

	R				
		peri[a]	*ortho*[b]	*peri*	*ortho*
XI	Br	−34 c/s	−61 c/s	−35 c/s[d]	−27 c/s[d]
XII	I	−33 c/s	−61 c/s	—	—
XIII	CN[c]	−32 c/s	−31 c/s	−24 c/s[d]	−24 c/s[d]
XIV	COOR	−83 c/s[e]	−59 c/s[e]	−63 c/s[f]	−43 c/s[f]
XV	5,6-dibromo	−42 c/s	—	—	—

[a,b] These values represent the difference in chemical shift between the perturbed protons and the unperturbed proton of ring A (a) or ring D (b).

[c] See Fig. 7. [d] Unpublished results (Brussels)

[e] Methyl ester [f] Ethyl ester, see Ref. 8.

II.3 *Benzo* [b] *biphenylenes disubstituted at positions* 5 *and* 10

As was expected, the protons of ring D give distinct multiplets (A_2B_2 system in the case of the 5,10-dibromoderivative VIII) because of the *peri* effects of the substituents on H_6 and H_9.

II.4 *Benzo* [a] *biphenylenes substituted at position* 5

The spectra of these derivatives are closely related. They all show a multiplet centered near 393 c/s, containing the four protons of ring D, and a multiplet near 438 c/s corresponding to the three protons ($H_{1,2,3}$) of ring A.

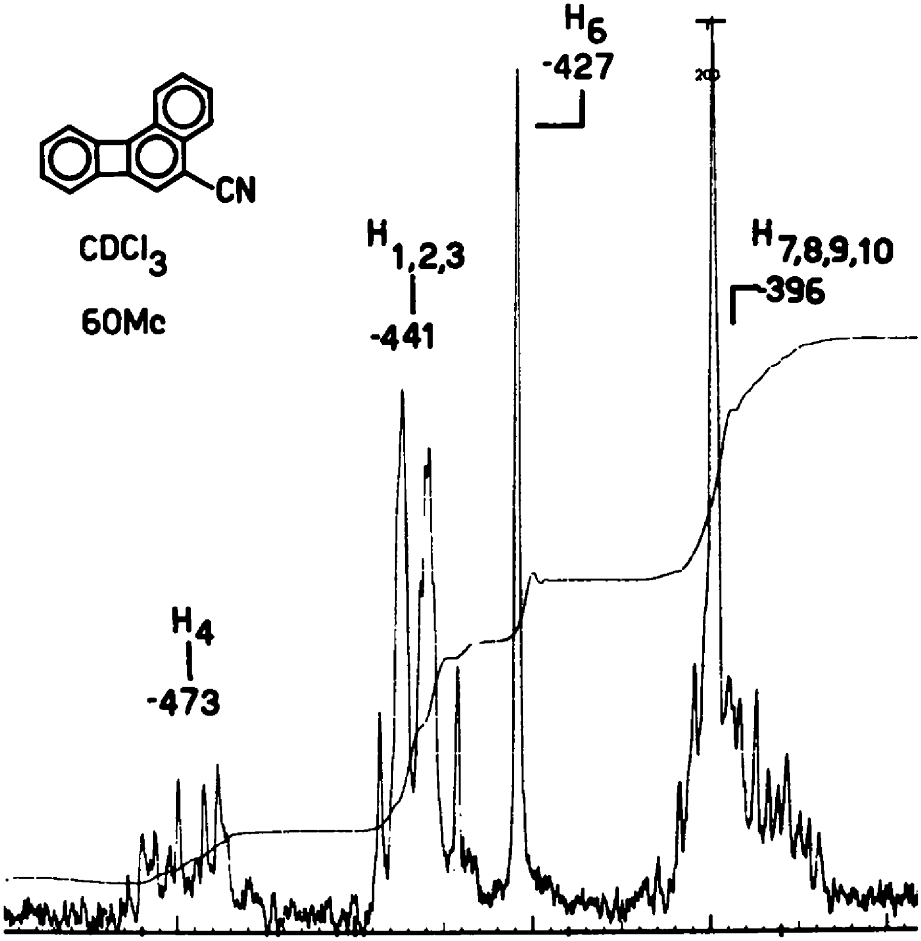


FIG. 7

We arrived at this conclusion by comparison with the spectrum of benzo [b] biphenylene and by the study of the cyano derivative (XIII). Considering the known deshielding effect of a cyano group on *ortho* protons and the occurrence of the H_6 singlet between the two multiplets of the unperturbed protons in the spectrum of

5-cyanobenzo [a] biphenylene (Fig. 7), it is clear that H_6 must "come out" of the high field multiplet. The spectra of the other derivatives are very simple to interpret on this basis.

In this series, *ortho* and *peri* effects are generally greater than in the purely benzenoid derivatives (e.g. see Table 3). The *ortho* effect of bromine is nevertheless exceptionally large in 5-bromobenzo [a] biphenylene (XI). This seems to indicate that the deshielding in the *ortho* position due to bromine is particularly sensitive to the valence bond order of the C—C bond in the unsubstituted hydrocarbon (e.g. C_5—C_6 in benzo [a] biphenylene). We are presently examining this problem in more detail.

CONCLUSIONS

The above examples show clearly that integrated NMR spectra can be of great help for structural determinations in the field of substituted biphenylenes, benzo [a] biphenylenes and benzo [b] biphenylenes.

Possible correlations between our experimental results and theoretical parameters are being investigated by Dr. J. Nasielski in collaboration with E. Germeyn in Brussels.

The spectra described in this paper were recorded on an A 60 (60 Mc) VARIAN spectrograph. The $CDCl_3$ solutions were either of the order of 8% (w/v) or, for the very insoluble derivatives, saturated solutions at 25°. With the exception of 5-iodo-, 5-cyano- and 5-methoxycarbonyl-benzo [a] biphenylene, which were prepared by one of us (J. P. V. T.) in Brussels, all the compounds used in this work were synthesized in Bristol.

Methyl 5-bromobenzo [b] *biphenylene-10-carboxylate* (IX). Treatment of 5,10-dibromobenzo [b] biphenylene first with n-butyllithium then with carbon dioxide[11] gave a mixture of mono- and dicarboxylic acids. This mixture was esterified with diazomethane and the bromo ester (IX) was isolated by chromatography on alumina (benzene). The bromo ester forms pale yellow crystals, m.p. 173–174° (Found: C, 63·9; H, 3·2; Br, 23·95; $C_{18}H_{11}BrO_2$ requires: C, 63·7; H, 3·3; Br, 23·6%).

We are grateful to Mr. R. Polain (Brussels) who has recorded the spectra. The Belgium authors are indebted to the "Fonds National de la Recherche Scientifique" (FNRS) for a grant to purchase the spectrograph and to the "Fonds de la Recherche Scientifique Fondamentale Collective" for financial support.

One of us (J. P. V. T.) expresses his gratitude to the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" (IRSIA) for the award of a fellowship.

Note: At the suggestion of a referee, we have recorded the spectra of 1-valeryl- and 1-methoxycarbonyl-biphenylene ($CDCl_3$, 60 Mc, TMS = 0).

XVI. 1-COC_4H_9n: δH_2 −432,5 [$J_{2,3} = 7{\cdot}3$, $J_{2,4} = 2{\cdot}3$], δH_3–H_8 −404·5 (I = 25), δCH_2 −167 and −91, δCH_3 −57 c/s.

XVII. 1-CO_2CH_3: δH_2 −432·5 [$J_{2,3} = 7{\cdot}0$, $J_{2,4} = 2{\cdot}5$], δH_3–H_8 −405 (I = 22), δCH_3 −233 c/s.

These results show that the *measured* coupling constants $J_{2,3}$ (1-$COCH_3$ II, 1-COC_4H_9n XVI, 1-CO_2CH_3 XVII) and $J_{3,4}$ (2-$COCH_3$ III, 2-CO_2CH_3 IV) are of the same magnitude (7·0–7·3 c/s).

The former ($J_{2,3}$) are smaller than the true coupling constants while the latter ($J_{3,4}$) are very close to the correct values.

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[11] cf. F. R. Jensen and W. E. Coleman, *Tetrahedron Letters* No. 20, 7 (1959).