Tetrahedron Vol 32, pp. 2571 to 2578. Pergamon Press 1976. Printed in Great Britain

EXPERIMENTAL AND THEORETICAL STUDY OF THE INDUCED PARAMAGNETIC RING-CURRENT IN THE 4-MEMBERED RING OF BIPHENYLENE AND RELATED HYDROCARBONS

H. P. FIGEYS,* N. DEFAY and R. H. MARTIN
Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, 50 Av. F. D. Roosevelt, 1050 Bruxelles, Belgique

and

J. F. W. MCOMIE,* B. E. AYRES and J. B. CHADWICK
School of Chemistry, The University, Bristol BS8 1TS

(*Received in the UK* 8 *March* 1976; *Accepted for publication* 22 *March* 1976)

Abstract—Ring current intensities and proton chemical shifts have been calculated for a series of condensed aromatic hydrocarbons including biphenylenes. The calculations show that an induced paramagnetic ring current occurs in the 4-membered ring of each of the biphenylenes studied and this effect accounts for the observed spectra. PMR measurements on 1-mono-, 2-mono- and 2,3,6,7-tetra-deuteriated biphenylene prove that the chemical shifts of the 1- and 2-protons are at δ_{CDCl_3} 6.60 and 6.70 respectively and not *vice versa* as assumed by previous authors.

During the last few years there have been several theoretical studies on the observed proton chemical shifts in condensed polycyclic benzenoid hydrocarbons.[1] These protons all appear at lower fields relative to the benzene resonance and this fact has been attributed to the joint deshielding action of the individual diamagnetic π-electron ring-currents in each of the rings of these molecules. In 1964, however, it was found that the protons of biphenylene appear at a *higher* field than for benzene,[2,3] and the same is true for certain protons of the benzobiphenylenes.[3,4] This behaviour can be due either to the occurrence of very low diamagnetic ring-currents in some rings of these molecules or to the presence of a *paramagnetic* ring-current in the four-membered ring exercising a substantial *shielding* effect on the surrounding protons and thus partially "quenching" the deshielding produced by the benzene rings. Such "reverse" ring-current effects have been observed in monocyclic annulenes and dehydroannulenes of the 4n π-electron series[5] and have been discussed by one of us in preliminary communications and an extensive review.[6] We now report the details of our theoretical and experimental evidence in favour of the second alternative, i.e. the presence of paramagnetic ring-currents.

RESULTS AND DISCUSSION

According to McWeeny's LCAO theory[7,8] of ring-current contributions to the proton chemical shifts in cyclic conjugated molecules we may write:

$$\delta(\text{ppm}) = \delta_0 + \frac{2\beta_0}{3}\cdot\left(\frac{2\pi e}{hc}\right)^2\cdot\frac{S^2\cdot 10^{-6}}{a^3}\cdot\sum_{\mu} J_\mu\cdot K_\mu \qquad (1)$$

where δ_0 is the resonance frequency of an olefinic proton in a similar environment, S the area of the benzene ring, β_0 the benzene exchange integral, a the length of the benzene C–C bond, J_μ the ring-current intensity of ring μ, and K_μ a distribution function of the effect of its anisotropy in space. Ring-current intensities were calculated for the series of hydrocarbons shown in Fig. 1 by the iterative self-consistent-β Hückel-theory developed previously.[9] The bonds in the 4-membered ring joining two benzene rings in the biphenylene compounds were considered, however, to have a constant bond-length of 1.52A,[10] to which a β-value of $0.84\beta_0$ was associated,[9] and no iterations were performed on this resonance integral.

A plot of δ_{obs}(ppm) against $\sum_{\mu} J_\mu\cdot K_\mu$ for the series of protons of the polycyclic benzenoid hydrocarbons yields a straight line (Fig. 2) from which, according to eqn (1), the following values can be determined:

$$\delta_0 = 5.727\ \text{ppm}$$
$$\beta_0 = 34.092\ \text{kcal/M}.$$

These values are in fair agreement with accepted estimates[1] for δ_0 and with recent thermodynamic data[11] for β_0. From these values and eqn (1), good predictions of the chemical shifts of the protons of other polycyclics, e.g. perylene could be made (Table 1). Similar calculations for the biphenylene series of molecules revealed several interesting features (Table 2). The most striking result is the occurrence of an induced paramagnetic ring-current in the 4-membered ring of all these compounds. Table 3 shows that a relation exists between the localisation of the π-electrons *in and around* the 4-membered ring (as given by the corresponding bond orders) and the magnitude of the ring-current. Clearly a "tetramethylenecyclobutane-like" structure with high exocyclic bond-orders, P_3, lowers the anti-aromaticity of the ring while it is enhanced in "cyclobutadiene-like" structures having highly localised double bonds *inside* the 4-membered ring. The first feature is favoured by linear annelation of benzene rings on the biphenylene nucleus and the second by angular annelation thus paralleling the known stabilities of these compounds.[12] Table 2 shows also that the diamagnetic ring-current of the benzene rings adjacent to the 4-membered ring is much reduced compared with the values generally observed in polycyclic benzenoid hyd-

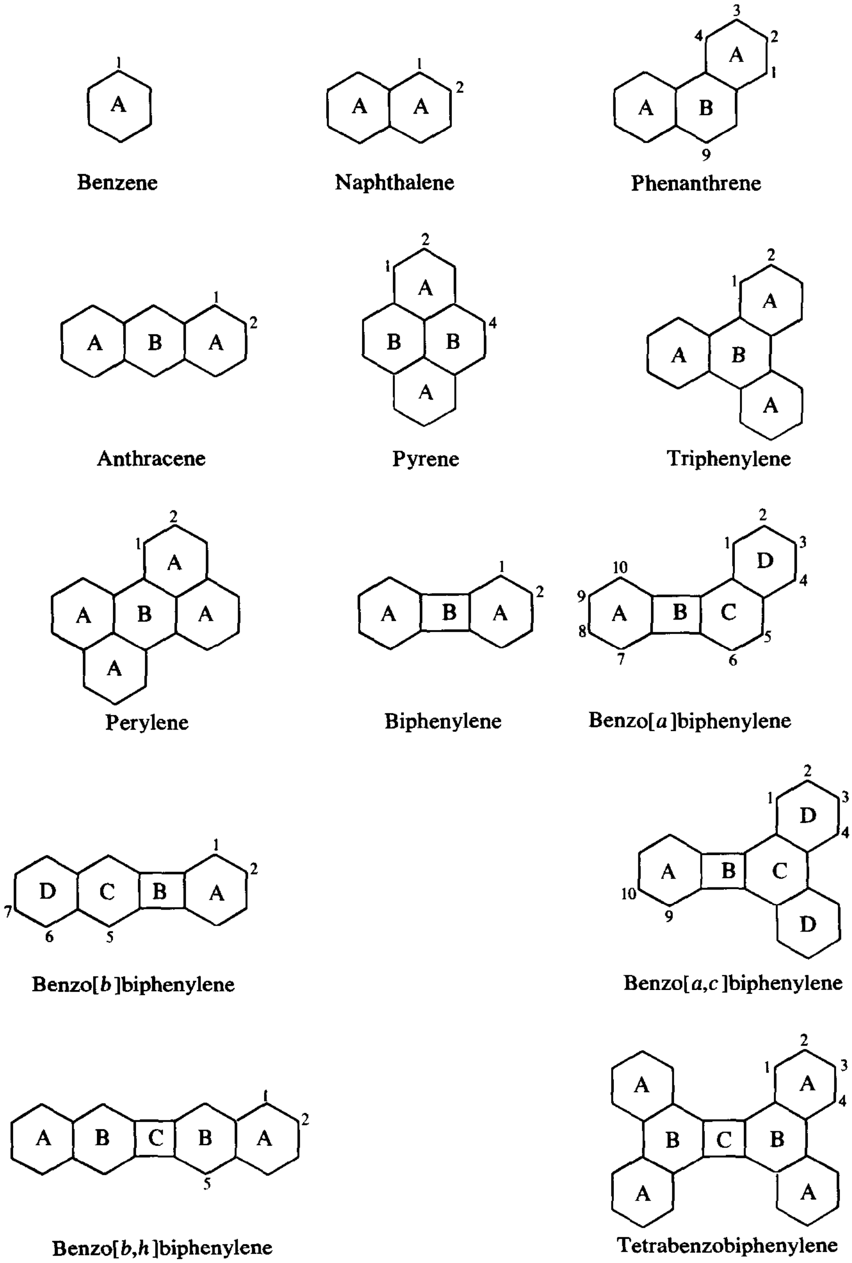

Benzene
Naphthalene
Phenanthrene
Anthracene
Pyrene
Triphenylene
Perylene
Biphenylene
Benzo[*a*]biphenylene
Benzo[*b*]biphenylene
Benzo[*a,c*]biphenylene
Benzo[*b,h*]biphenylene
Tetrabenzobiphenylene

Fig. 1. Ring identification and proton numbering of the hydrocarbons studied.

rocarbons (Table 1). This reduction is most probably due to the bond-length alternation[13] in the benzene rings caused by the 4-membered ring, as can be seen from the bond-order values shown in Table 4. Undoubtedly the high-field resonances observed for some aromatic protons in the benzo-biphenylene series of compounds are due to the joint influence of the two effects mentioned above.

The PMR spectrum of benzo[*b*]biphenylene described by Martin *et al.*[3] provides experimental evidence for an induced paramagnetic ring-current in the 4-membered ring of this molecule. The spectrum shows a broad singlet at 6.91 ppm which has been assigned, by comparison with the spectra of substituted benzo[*b*]biphenylenes, to protons 1–5 and 10: protons 6–9 give a typical AA'BB' multiplet centred at 7.30 ppm. However, according to the hypothesis of deshielding ring-currents, δH_1 should appear at a lower field than δH_2, whatever the relative values of the individual ring-currents, owing to the closer proximity of rings B, C and D. The only way to explain the experimental observations is to postulate an induced paramagnetic ring-current in the 4-membered ring whose difference of shielding effect on protons 1 and 2 is almost exactly compensated by the difference in deshielding effects of rings C and D. Table 2 shows that the agreement between calculated and experimental chemical shifts for biphenylene derivatives is less good than for polycyclic benzenoid hydrocarbons but that, within the same molecule, trends are respected; in the case of benzo[*b*]biphenylene previous attributions[3] are confirmed.

The chemical shifts calculated for the biphenylene protons, however, (Table 2) suggest that proton 2 is more deshielded than proton 1: the contributions δ_{RC} of the different rings to the calculated chemical shifts are given

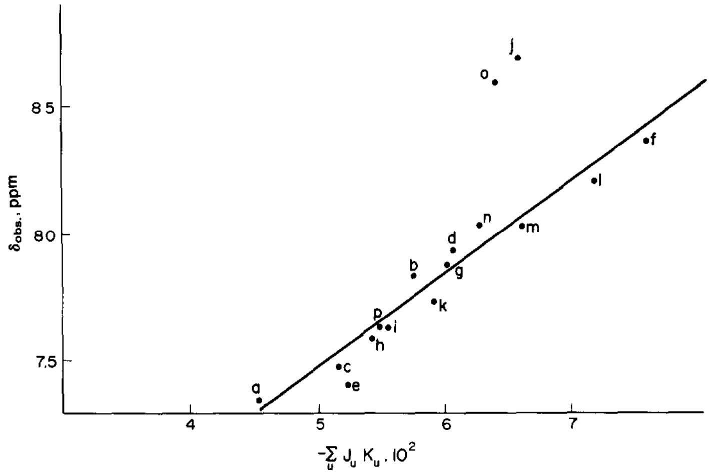


Fig. 2. Relation between observed chemical shift and ring-current effects. Benzene proton = a; naphthalene: H_1 = b, H_2 = c; anthracene: H_1 = d, H_2 = e, H_9 = f; phenanthrene: H_1 = g, H_2 = h, H_3 = i, H_4 = j, H_9 = k; pyrene: H_1 = l, H_2 = m, H_4 = n; triphenylene: H_1 = o, H_2 = p.

Table 1. Ring-currents, calculated and observed proton chemical shifts in polycyclic benzenoid hydrocarbons

Molecule	Ring-Current		Proton	Chemical Shifts*		Difference
	Ring	Intensity		Observed	Calculated	
Benzene	A	0.1113	1	$7.342^{\dagger}$	7.282	0.060
Naphthalene	A	0.1198	1	7.81	7.729	0.081
			2	7.46	7.522	-0.062
Phenanthrene	A	0.1248	1	$7.855^{\ddagger}$	7.821	0.033
	B	0.1042	2	$7.570^{\ddagger}$	7.615	-0.045
			3	$7.612^{\ddagger}$	7.653	-0.041
			4	$8.648^{\ddagger}$	$8.021^{\$}$	0.627
			9	$7.702^{\ddagger}$	7.649	0.052
Anthracene	A	0.1177	1	7.91	7.835	0.075
	B	0.1414	2	7.39	7.546	-0.156
			9	8.31	8.348	-0.037
Pyrene	A	0.1459	1	8.16	8.214	-0.054
	B	0.1031	2	7.99	8.021	-0.031
			4	8.06	7.915	0.145
Triphenylene	A	0.1218	1	8.56	$7.963^{\$}$	0.593
	B	0.0779	2	7.61	7.629	-0.019
Perylene	A	0.1074	1	8.162	$7.691^{\$}$	0.471
	B	0.0235	2	7.482	7.446	0.036
			3	7.672	7.608	0.064

[*] In ppm with respect to TMS; experimental values obtained from N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys. 36, 2443 (1962), unless otherwise stated.

[†] Obtained from Ref. 8.

[‡] R.C. Fahey and G.C. Graham, J. Phys. Chem. 69, 4417 (1965).

[\$] Discrepancy between experimental and calculated shift is due to a mutual Van der Waals effect between the bay protons.

in Table 5. As shown in Fig. 3, the PMR spectrum of biphenylene is a very compact AA'BB' system from which it is impossible to tell *a priori* which of the two sets of protons, α or β, appears at lower field. Katritzky and Reavill[2] tried to assign the individual shifts by selective deuteration of biphenylene with deuterio-trifluoroacetic acid in carbon tetrachloride at 34°. Portions of the mixture were evaporated to dryness at intervals and the PMR spectra were measured. The authors claimed that successive spectra of the partially deuterated biphenylene showed that the *high-field* side of the AA'BB' pattern lost intensity first. Since the 2-position is known to be more reactive to electrophilic substitution than the 1-position,[14] they concluded that the high-field half of the spectrum is due to the β-protons. The disagreement between this assignment and our theoretical predictions led us to repeat the deuteration experiment in an NMR tube. Spectral changes were followed by the repeated scanning of a solution of 39.3 mg of biphenylene in 0.5 ml of carbon tetrachloride to which 0.21 ml of deuterio-trifluoroacetic acid was added in three portions. Contrary to Katritzky's statement, the *low-field* part of the spectrum gradually lost intensity and disappeared almost completely after 4 h.

In order to settle the problem conclusively, we studied the PMR spectra of three deuterated biphenylenes of known structures. The synthesis of these is given in the Experimental section. The PMR spectra of biphenylene, also 1- and 2-deuteriobiphenylene, measured under

Table 2. Ring-currents, calculated and observed proton chemical shifts in biphenylenes

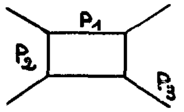
Molecule	Ring-current Ring	Ring-current Intensity*	Proton	Chemical shift† Observed	Chemical shift† Calculated
Biphenylene	A	0.514	1	6.60	6.34
	B	-1.166	2	6.70	6.49
Benzo [a] biphenylene	A	0.370	1	centered at 7.25	7.20
	B	-1.479	2		7.13
	C	0.700	3		7.14
	D	0.871	4		7.27
			5		7.02
			6	6.88	6.64
			7	centered at 6.47	6.09
			8		6.27
			9		6.28
			10		6.14
Benzo [b] biphenylene	A	0.574	1	6.91	6.52
	B	-0.952	2	6.91	6.61
	C	0.572	5	6.91	6.76
	D	0.925	6	7.43	7.33
			7	7.23	7.23
Benzo [a,c] biphenylene	A	0.281	1	centered at 7.5	7.41
	B	-1.675	2		7.35
	C	0.717	3		7.38
	D	0.991	4	8.4	7.69‡
			9	centered at 6.5	6.00
			10		6.16

*Ring-current intensity of benzene taken as unity.

†In ppm with respect to TMS.

‡Due to a mutual Van der Waals effect between the bay protons, a deshielding of 0.5-0.6 ppm (see Table 1) should be added to this value.

Table 3. Mean π-bond-orders and ring-current in the four-membered ring of some biphenylene derivatives



Molecule	Bond-Orders P_1	Bond-Orders P_2	Bond-Orders P_3	Ring-current*
Benzo [b,h] biphenylene	0.267	0.503	0.735	-0.777
Benzo[b]biphenylene	0.247	0.542	0.709	-0.952
Biphenylene	0.219	0.587	0.686	-1.166
Benzo[a]biphenylene	0.210	0.603	0.644	-1.479
Benzo [a,c]biphenylene	0.201	0.645	0.608	-1.675
Tetrabenzobiphenylene	0.165	0.712	0.530	-2.827

* Ring-current intensity of benzene taken as unity.

identical conditions, are compared in Fig. 3. Clearly, deuteration in the 1-position lowers the intensity at the high-field side of the spectrum while the converse is observed for deuteration in the 2-position: this has been confirmed by calculation of the corresponding seven proton spectra using the LAOCOON-computer program of Castellano and Bothner-By.[15] Moreover, Fig. 4 shows that in the PMR spectrum of 2,3,6,7-tetra deuterio-biphenylene the signal for the remaining *α-protons* appears as a broad singlet at the high-field side of the biphenylene AA'BB' multiplet. We therefore conclude that the α-protons are less deshielded then the β-protons, in agreement with the theoretical predictions but contrary to previous statements.[2]

EXPERIMENTAL

The deuteriated biphenylenes were made from 99.7% D_2O using the method of Chenon *et al.*[16] The CaO was dried for 2 hr at 600°/0.05 mm before use. The Zn dust was washed three times

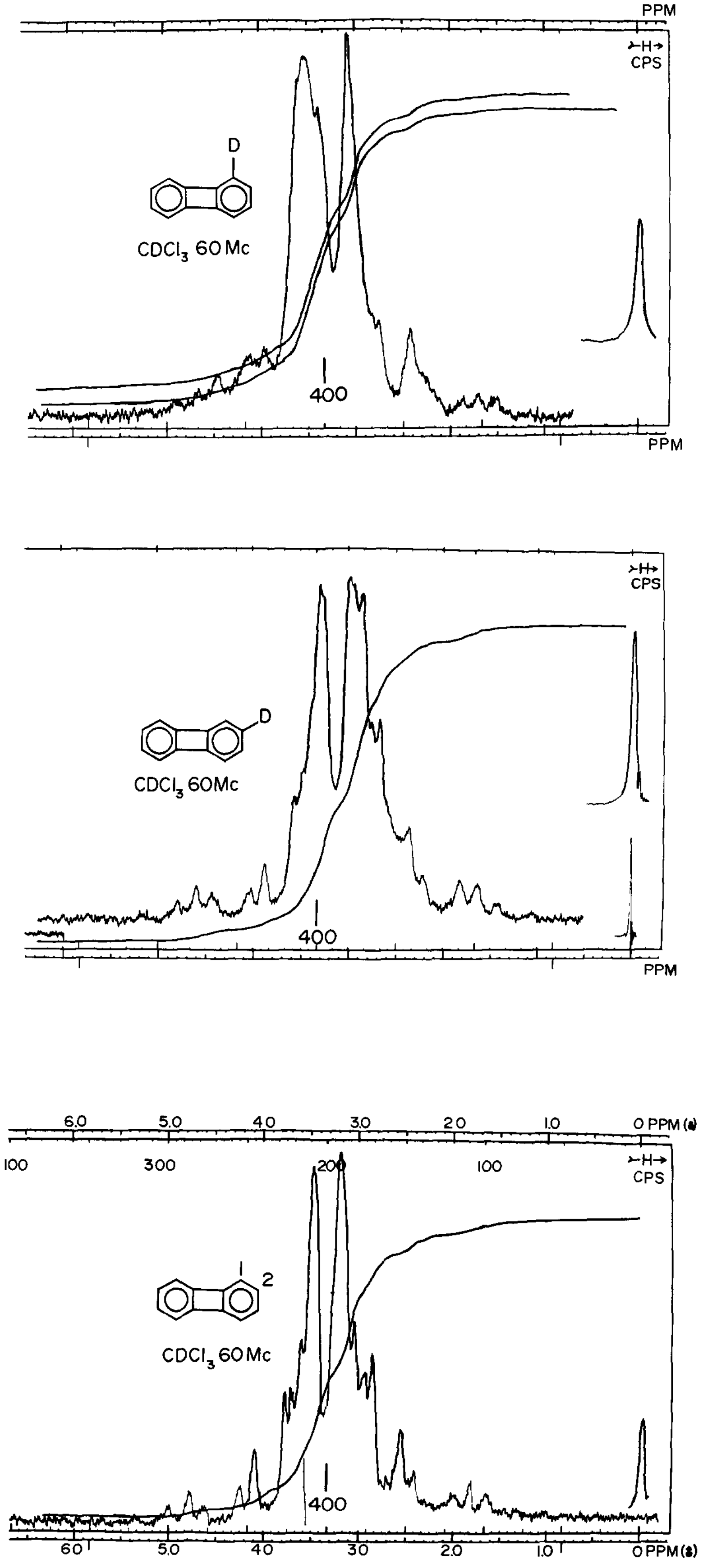
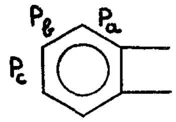


Fig. 3. PMR spectra of 1-deuterio-, 2-deuterio-, and unsubstituted biphenylene in $CDCl_3$ solution at 60 MHz.

Table 4. π-Bond-orders and Ring-current in the mono-condensed benzene ring of some biphenylene derivatives

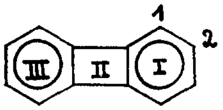


Molecule	Bond-orders			Ring-Current*
	P_a	P_b	P_c	
Benzo[b]biphenylene	0.672	0.640	0.678	0.574
Biphenylene	0.686	0.628	0.690	0.514
Benzo[a]biphenylene	0.693†	0.618†	0.697	0.370
Benzo[a,c]biphenylene	0.700	0.609	0.704	0.281

* Ring-current of benzene taken as unity.

† mean values.

Table 5. Contributions of the different rings to the calculated chemical shifts of protons 1 and 2 in biphenylene



Proton	Ring I	$\delta_{R.C.}$ (ppm) Ring II	Ring III	Total contribution (ppm)
1	0.802	-0.254	0.062	0.610
2	0.802	-0.062	0.024	0.764

with ethanol and then three times with ether before being dried at 100°/0.05 mm. IR spectra were measured in Nujol mulls.

1-*Deuteriobiphenylene*. A mixture of 1-iodobiphenylene[17] (204 mg), CaO (218 mg), Zn dust (2.09 g) and D_2O (5 ml) was refluxed, with stirring, for 24 hr. The mixture was extracted with ether (3 × 5 ml) and gave 1-deuteriobiphenylene (86 mg, 77%) as a pale yellow solid, which after being sublimed at 50°/0.1 mm had m.p. 110–112°, IR 705s, 740s, 745s and 780s cm^{-1}. The isotopic purity was >97% (mass spec.).

2-*Deuteriobiphenylene*. This was made as above from 2-iodobiphenylene[18] (251 mg), CaO (269 mg), Zn dust (2.8 g), and D_2O (7 ml). The 2-deuteriobiphenylene (118 mg, 86%) was sublimed at 50°/0.1 mm and then had m.p. 110–112°, IR 740s, 750s, 855s cm^{-1}. The isotopic purity was >97% (mass spec.).

2,3,6,7-*Tetrabromobiphenylene*

(a) Powdered biphenylene (1.5 g), spread on a watch-glass, was placed in the upper part of a desiccator containing bromine (6.8 g) in the lower part, and the whole was kept in a dark cupboard for 12 hr. The resulting orange, oily solid was dissolved in chloroform and washed successively with aqueous $NaHCO_3$, aqueous $NaHSO_3$ and water. Removal of the chloroform gave an oily solid which on recrystalisation from benzene gave 2,3,6,7-*tetrabromo biphenylene* (0.48 g, 10%) as yellow granules, m.p. 300° (dec.) (Found: C, 30.9; H, 1.0. $C_{12}H_4Br_4$ requires: C, 30.8; H, 0.9%), UV (EtOH) λ_{max} 234 (log ϵ 4.27), 250sh (4.62), 259 (4.97), 267 (5.16), 358 (4.15), and 377 (4.21), IR 868s cm^{-1}.

(b) (Method of Brown *et al.*[19]). 4,5-Dibromophthalic anhydride[20] (5 g) was sublimed through a silica tube (35 × 2.6 cm i.d.) at 800° during 45 min. The pressure rose gradually from 0.1 to 1.5 mm during this time. The pyrolysis product was extracted with $CHCl_3$ and the solution was stirred overnight with 2N NaOH to remove unchanged anhydride. The chloroform soln was then evaporated and the residue recrystallised from benzene (charcoal) to give 2,3,6,7-tetrabromobiphenylene (33 mg, 0.9%), m.p. 295–298° (dec.) identical (UV and IR) with that prepared by method (a). The mother liquors from the recrystallisation yielded 1,2,4,5-tetrabromobenzene (204 mg, 3%) as needles, m.p. 179–180° (from ethanol) (lit.[21] m.p. 174°). (Found: C, 18.6; H, 0.9. Calc. for $C_6H_2Br_4$: C, 18.3; H, 0.5%).

(c) (With Dr. T. P. Prabhu). Biphenylene (0.6 g) was dissolved in conc. H_2SO_4 (3 ml) and kept at room temp. for 24 hr. The mixture, containing biphenylene-2,6-disulphonic acid,[22] was poured into water (40 ml) in a conical flask fitted with a dropping funnel and a reflux condenser. Br_2 (0.8 ml) in AcOH (2 ml) was added dropwise during 30 min and the mixture was stirred at 70° for 3 hr. The ppt was collected and recrystallised from benzene to give 2,3,6,7-tetrabromobiphenylene (0.11 g, 6%) m.p. 305° (dec), identified by analysis, UV and IR.

2,3,6,7-*Tetradeuteriobiphenylene*

(a) A mixture of 2,3,6,7-tetrabromobiphenylene (350 mg), CaO (1 g), Zn dust (10 g), and D_2O (15 ml) was refluxed, with stirring, for 48 hr. The organic product was collected in ether and purified

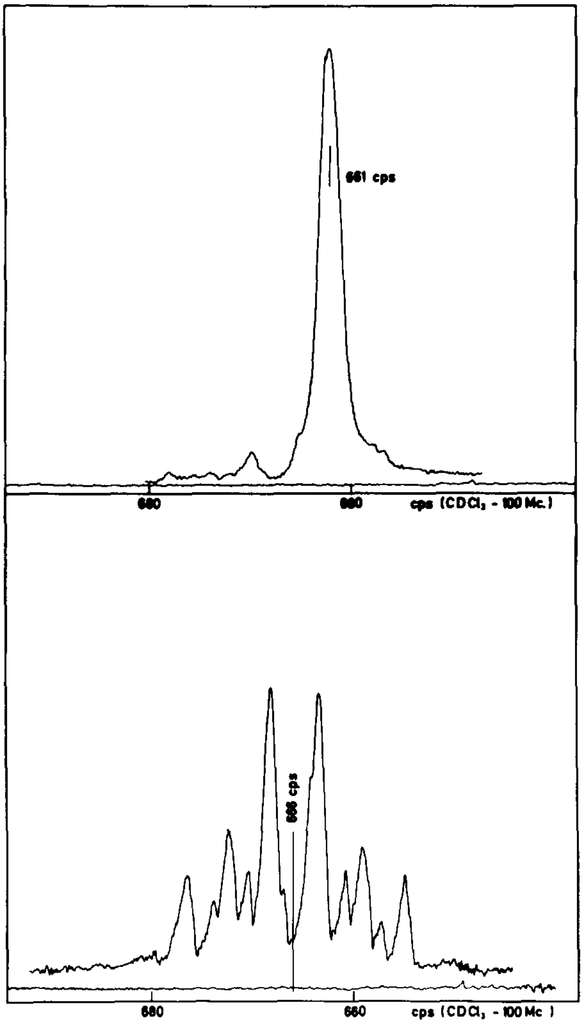


Fig. 4. PMR spectra of 2,3,6,7-d_4-biphenylene (upper) and unsubstituted biphenylene (lower) in $CDCl_3$ solution at 100 MHz.

by sublimation at 70°/20 mm to give 2,3,6,7-tetradeuteriobiphenylene (25 mg, 22%) as needles, m.p. 106° (subl.), (Found: M^+ 156. $C_{12}H_4D_4$ requires: 156). The IR spectrum showed only one band (896 m) between 700 and 900 cm^{-1}.

(b) (Method of Lunelli and Pecile[23]). Biphenylene (160 mg) and $F_3C{\cdot}CO_2D$ (3 g) were heated under reflux for 18 hr. The black solid was collected by filtration and washed with D_2O. The filtrate was diluted with D_2O and the resulting grey ppt was collected. The IR spectra of the two solids was identical, showing peaks at 740w, 855vs cm^{-1}. The combined solids were sublimed at 90°/20 mm and gave 2,3,6,7-tetradeuteriobiphenylene (85 mg, 52%) m.p. 110–112°. The IR spectrum was identical with that from the authentic compound made by method (a) except that it contained a peak at 855w cm^{-1} corresponding to 2 adjacent aryl hydrogens. The mass spectrum showed a base peak at M^+ 156 ($C_{12}H_4D_4$) but the peak 155 was more intense than that of the compound made by method (a). Thus, although the compound is mainly 2,3,6,7-deuteriobiphenylene it contains some trideuteriobiphenylene. The PMR spectrum showed a multiplet at 6.75–7.0 ppm with a very large peak at 6.61 ppm.

Acknowledgements—The authors are grateful to Dr. M. Kaisin (Bruxelles) for measuring the deuterium content of 1- and 2-deuteriobiphenylene and to Elek Books, London, for permission to reproduce Figs. 3 and 4 from *Topics in Carbocyclic Chemistry*, Vol. 1. Logos Press, London (1969). They are particularly indebted to the Université Libre de Bruxelles for a generous computer grant in support of this work.

REFERENCES

[1] C. W. Haigh, R. B. Mallion and E. A. G. Armour, *Mol. Phys.* **18**, 751 (1970); and refs therein.

[2] A. R. Katritzky and R. E. Reavill, *Rec. Trav. Chim.* **83**, 1230 (1964); G. Fraenkel, Y. Asahi, M. J. Mitchell and M. P. Cava, *Tetrahedron* **20**, 1179 (1964).

[3] R. H. Martin, J. P. Van Trappen, N. Defay and J. F. W. McOmie, *Ibid.* **20**, 2373 (1964).

[4] J. W. Barton, A. M. Rogers and M. E. Barney, *J. Chem. Soc.* 5537 (1965); J. W. Barton and S. A. Jones, *Ibid.* 1276 (1967).

[5] See, for example, R. C. Haddon, V. R. Haddon and L. M. Jackman, *Topics in Current Chemistry* **16**, 1–118 (1971); J. F. M. Oth, *Pure Appl. Chem.* **25**, 573 (1971); F. Sondheimer, *Acc. Chem. Res.* **5**, 81 (1972).

[6] H. P. Figeys, *Chem. Comm.* 495 (1967); *Angew Chem.* Intern. Edn. **7**, 642 (1968); *Topics in Carbocyclic Chemistry* (Edited by D. M. G. Lloyd), Vol. 1, pp. 269–359. Logos Press, London (1969).

[7] R. McWeeny, *Mol. Phys.* **1**, 311 (1958); A. Veillard, *J. Chim. Phys.* **59**, 1056 (1962); J. D. Memory, *J. Chem. Phys.* **38**, 1341 (1963).

[8] H. P. Figeys, *Tetrahedron Letters* 4625 (1966).

[9] H. P. Figeys and P. Dedieu, *Theor. Chim. Acta* **9**, 82 (1967).

[10] J. K. Fawcett and J. Trotter, *Acta Cryst.* **20**, 87 (1966); A. Yokozeki, C. F. Wilcox and S. H. Bauer, *J. Am. Chem. Soc.* **96**, 1026 (1974).

[11] H. P. Figeys, *Tetrahedron* **26**, 4615 (1970).

[12] H. P. Figeys, C. D'Hayer and A. Dralants, to be published.

[13] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.* **88**, 4811 (1966); F. Bear, H. Kuhn and W. Regel, *Z. Naturforsch.* **22A**, 103 (1967).

[14] See, for example, J. W. Barton, *Nonbenzenoid Aromatics* (Edited by J. P. Snyder), Vol. 1, pp. 31–62. Academic Press, New York (1969); A. Streitwieser, A. Lewis, I. Schwager, R. W. Fish and S. Labana, *J. Am. Chem. Soc.* **92**, 6525 (1970).

[15] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.* **41**, 3863 (1964).

[16] B. Chenon, L. C, Leitch, R. N. Renaud and L. Pichat, *Bull. Soc. chim. France* 38 (1964).

[17] J. W. Barton and K. E. Whitaker, *J. Chem. Soc.* (C), 28 (1968).

[18] W. Baker, J. W. Barton and J. F. W. McOmie, *Ibid.* 2666 (1958).

[19] R. F. C. Brown, D. V. Gardner, J. F. W. McOmie and R. K. Solly, *Austral. J. Chem.* **20**, 139 (1967).

[20] T. Zincke and K. Fries, *Liebigs Ann.* **334**, 366 (1904).

[21] R. L. Datta and J. C. Bhoumik, *J. Am. Chem. Soc.* **43**, 312 (1921).

[22] W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.* 1476 (1954).

[23] B. Lunelli and C. Pecile, *Can. J. Chem.* **46**, 391 (1968).