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POLYCYCLIC BIPHENYLENES. PART V.[1] THE PMR SPECTRA OF ANNELATED BIPHENYLENES

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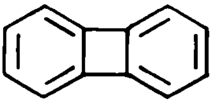
Abstract - The proton magnetic resonance spectra of a number of annelated biphenylenes are given. The influences of ring currents and bond-localisation effects are demonstrated.

The proton magnetic resonance (pmr) spectra of aromatic systems have been widely studied and interpreted in relation to the ring currents sustained by the π-systems of the molecules.[2] Studies of annulenes have been confined mainly to monocyclic compounds,[3,4] polycyclic systems such as biphenylene (1) have been less well investigated.



(1)

Biphenylene (1) is formally a tricyclic [6][4][6] annulene with fused aromatic : antiaromatic : aromatic rings, the chemical properties of which reflect to some extent the influences of strain and of antiaromatic character of the central four-membered ring.[5] In the pmr spectrum, it is found that the protons of (1) resonate at higher field than those of benzene, and this effect can be attributed to two interrelated causes:

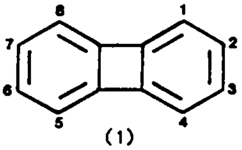
i) Reduced diamagnetic ring currents in the six-membered rings due to bond localisation, i.e. a 'methylenecyclobutane' structure for (1).

ii) The existence of an induced paramagnetic ring current in the four-membered ring, i.e. a 'dibenzocyclobutadiene' structure for (1).

The part-localised nature of the benzenoid rings of (1) has been demonstrated by X-ray measurements, which have shown that the C_1-C_2 bond length is greater than that of C_2-C_3,[6,7] and by analysis of its pmr spectrum, which has shown that $J_{2,3} > J_{1,2}$.[8,9]

The existence of an induced paramagnetic ring current in the central ring of (1) is implied by the observation that H_1, adjacent to the four-membered ring, resonates at higher field than H_2. These assignments were confirmed by Figeys et al.[3,10] using deuterium labelling, subsequent to earlier conflicting reports.

The pmr spectra of annelated biphenylenes have been little studied, only low resolution spectra of benzo[a]biphenylene (2), benzo[b]biphenylene (3) and dibenzo[a,c]biphenylene (4) have been calculated by Figeys et al.[3,10] and compared with recorded spectra.[10,11] We present now the pmr spectra of a series of annelated biphenylenes, recorded on deuteriochloroform solutions of samples in the concentration range 0.3 – 0.04 M using a Jeol FX 200 instrument at ambient temperatures. The samples were available from earlier work.[1,11-15] The spectrum of dibenzo[b,h]biphenylene (5) could not be recorded due to its low solubility in deuteriochloroform. Except in the cases of biphenylene (1) and benzo[3,4]cyclobuta[1,2-b]biphenylene (8) no second-order analysis has been attempted and chemical shift values refer to the centre of each multiplet.

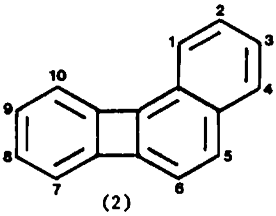


(1)

$H_{2,3,6,7}$	6.72(m)	AA'BB' System
$H_{1,4,5,8}$	6.62(m)	

$J_{1,2} = 6.89$ $J_{1,3} = 0.84$

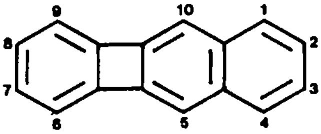
$J_{1,4} = 1.00$ $J_{2,3} = 8.27$



(2)

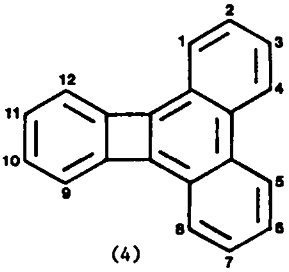
H_1 or H_4	7.52 (dd)	
H_4 or H_1	7.40 (dd)	
H_5	7.33 (d)	
H_2 or H_3	7.25 (td)	
H_3 or H_2	7.10 (td)	
H_6	6.93 (d)	
$H_{8,9,10}$	6.50 (m)	MABC System
H_7	6.41 (m)	

$J_{5,6} = 7.81$



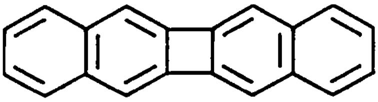
(3)

$H_{1,4}$	7.46 (m)	AA'BB' System
$H_{2,3}$	7.25 (m)	
H_{5-10}	6.93 (m)	

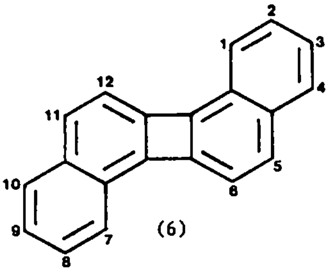


(4)

$H_{4,5}$	8.60 (m)	XMAB System
$H_{1,8}$	7.68 (m)	
$H_{2,3,6,7}$	7.55 (m)	
$H_{10,11}$	6.60 (m)	AA'BB' system
$H_{9,12}$	6.54 (m)	



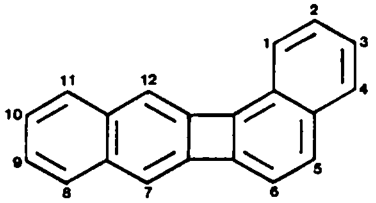
(5)



(6)

$H_{1,7}$ or $H_{4,10}$	7.58 (dd)
$H_{4,10}$ or $H_{1,7}$	7.43 (dd)
$H_{2,8}$ or $H_{3,9}$	7.24 (td)
$H_{5,11}$	7.23 (d)
$H_{3,9}$ or $H_{2,8}$	7.09 (td)
$H_{6,12}$	6.86 (d)

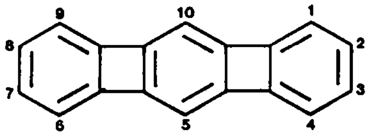
$J_{5,6} = 7.23$



(7)

$H_{1,4}$	7.66 (m)
H_5	7.52 (d)
$H_{2,3,8,11}$	7.35 (m)
$H_{9,10}$	7.20 (m)
H_6	7.15 (d)
H_{12}	6.85 (s)
H_7	6.72 (s)

$J_{5,6} = 8.06$

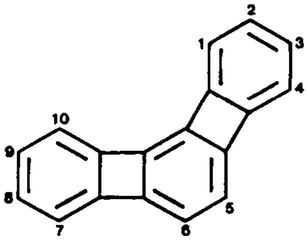


(8)

$H_{2,3,7,8}$	6.63 (m)	AA'XX' System
$H_{1,4,6,9}$	6.42 (m)	
$H_{5,10}$	6.24 (s)	

$J_{1,2} = 6.73$ $J_{1,3} = 0.78$

$J_{1,4} = 0.92$ $J_{2,3} = 8.37$



(9)

$H_{1-4,7-10}$	6.95 (m)	ABCD System
$H_{5,6}$	6.15 (s)	

Chemical shift (δ) values are ppm downfield from tetramethylsilane (internal) = 0.00; coupling constant (J) values are in Hertz.

The Chemical Shifts

The most obvious feature seen in the observed chemical shifts is that in all cases the biphenylene protons resonate at higher field than those of their component arenes, e.g. the protons of biphenylene (1) appear at higher field than those of benzene; those of the naphthalene moieties of the benzobiphenylenes (2) and (3) appear at higher field than those of naphthalene.[16] This effect is general and is not confined to those rings directly fused to the four-membered ring. Since the effect of a ring current decreases with the cube of the distance from the centre of the ring current,[2] it is difficult to rationalise the upfield shift of outer-ring protons (e.g. H_{1-4} of benzo[a]biphenylene (2) in terms of a paramagnetic ring current in the four-membered ring. The observed effect is probably a consequence of bond-localisation and concomitant reduction of the diamagnetic ring currents of the benzenoid rings of the annelated biphenylenes. In general, this effect is most pronounced in the angularly annelated biphenylenes.

The magnitude of the ring current effect can be assessed by examining the spectra of a series of compounds such as (2), (6) and (7). In the spectra of these compounds the signals for H_5 and H_6 appear as clearly-defined doublets. If the four-membered ring sustains an induced paramagnetic ring current then proton H_6, nearer to the four-membered ring, will resonate at higher field than H_5. If this ring current increases both H_5 and H_6 will exhibit an upfield shift and also the difference $\Delta_{5,6}$ will increase. The values for (2), (6) and (7) are tabulated below:

	H_5	H_6	$\Delta_{5,6}$
(7)	7.52	7.15	0.37
(2)	7.33	6.93	0.40
(6)	7.23	6.80	0.43

We conclude from these values that the paratropic nature of the four-membered rings in these compounds increases in the order (7)<(2)<(6), which is in line with their predicted cyclobutadienoid character and the observed stability pattern of the compounds, which decreases in the order (7)>(2)>(6).[17-20]

The Coupling Constants

As described earlier, in the spectra of (2), (6) and (7) H_5 and H_6 appear as clearly defined doublets. This allows $J_{5,6}$ to be measured directly and accurately. For a series of related compounds it has been shown[21] that the coupling constant, $J_{R,S}$, is proportional to the Hückel π-bond order, $P_{R,S}$, over the intervening C C bond, according to the relationship:

$$J_{R,S} = 12.7P_{R,S} - 1.1 \text{ (Hz)}$$

Assuming this proportionality to have some validity with respect to biphenylenes, $P_{5,6}$ can be calculated from $J_{5,6}$. These values are tabulated below:

	$J_{5,6}$	$P_{5,6}$
(7)	8.06	0.72
(2)	7.81	0.70
(6)	7.23	0.66

The values of $J_{5,6}$ and $P_{5,6}$ decrease in the order (7)>(2)>(6), thus the apparent effect of linearly annelating a further ring to (2) to give (7) is to increase the bond order at C_5-C_6 and conversely angular annelation to give (6) lowers this. In other words the part of the molecule containing C_5-C_6 is more bond-localised in (7) than in (6) and movement of proton resonances to higher field would be expected, due to reduced diamagnetic ring current effects in the six-membered rings. This bond-localisation effect should augment the shielding effect of the paramagnetic ring current of the four-membered ring. These effects are of course interrelated in that the magnitude of the paramagnetic ring current of the four-membered ring depends on the total π-bond order in the ring.

It is also noted that the signal for H_5 is broader than that for H_6, due to a small transannular coupling, either a peri-coupling with H_4, or an epi-coupling with H_1, as observed in other polycyclic hydrocarbons.[22]

The Sesquibiphenylenes

Recently we reported the synthesis of the linear sesquibiphenylene, benzo[3,4]cyclobuta[1,2-b]biphenylene (8),[15] an alternative synthesis of which has now been described.[23] In that report we briefly compared the nmr parameters of compound (8) with those of the angular isomer, benzo[3,4]cyclobuta[1,2-a]biphenylene (9), which had been synthesised earlier.[14] Pmr chemical shift values for (8), (9) and for biphenylene (1) are tabulated below:

	Ring Position					
	1	2	3	4	5	$\Delta_{1,2}$
(1)	6.62	6.72	6.72	6.62	-	-0.10
(8)	6.42	6.63	6.63	6.42	6.24	-0.21
(9)	6.95	6.95	6.95	6.95	6.12	0

The above data provide some evidence as to the bond structures of (8) and (9). The influence of paramagnetic ring currents in the four-membered rings is illustrated by the chemical shift difference $\Delta_{1,2}$ between H_1 and H_2 in each case. For the angular compound (9) this is virtually zero, the outer ring protons, H_{1-4}, resonating as a narrow ABCD multiplet in which individual resonances cannot be resolved, whereas for biphenylene (1) $\Delta_{1,2} = -0.10$ and for the linear compound (8) $\Delta_{1,2} = -0.21$. This leads to the conclusion that the paratropic nature of the four-membered rings increases in the order (9)<(1)<(8) which is in general agreement with HMO calculations.[20]

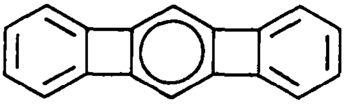
The anomalous shifts of the protons H_5 of the central rings of the sesquibiphenylenes may be explained on the basis of a high degree of bond-localisation in the central ring of the angular isomer (9). This allows delocalisation of the outer rings to occur without there being a high π-bond order in the four-membered rings. Thus H_5 resonates at very high field, in the region associated with vinylic protons. This is also consistent with the observation that the outer ring protons of (9) resonate at lower field than those of biphenylene (1), in the region associated with the aromatic protons of benzocyclobutenes,[24,25] a finding which could not be rationalised if large paramagnetic ring currents were present in the four-membered rings of (9).

Evidence for bond localisation in the outer rings of the linear compound (8) is given by the coupling constants around the ring, which are tabulated below together with those of biphenylene (1):

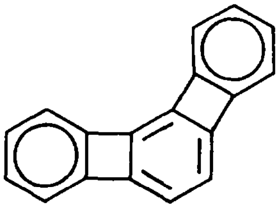
	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$
(1)	6.89	0.84	1.00	8.27
(8)	6.73	0.78	0.92	8.37

The increased value of $J_{2,3}$, and the reduced values of $J_{1,2}$ and the longer-range couplings, implies that the outer rings of (8) are less delocalised than those of (1), tending towards a 'cyclohexatriene' structure. A concomitant shift giving rise to higher field resonances also occurs, augmenting the shift due to paramagnetic ring currents in the four-membered rings.

Thus on the basis of evidence provided by the pmr spectra, the representations (8a) and (9a) are suggested as illustrating the contrast between the structures of (8) and (9).



(8a)



(9a)

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