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Electron Spin Resonance Spectroscopy of Radical Cations and Anions of Methylated Biphenylenes, Tetraphenylene, and Octa-β-methyltetraphenylene

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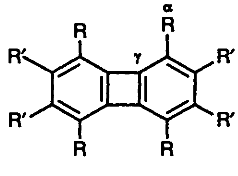
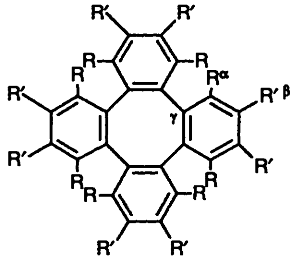
Octa-β-methyltetraphenylene has been prepared in low yield by the thermolysis of tetra-β-methylbiphenylene.

The radical cations and radical anions of tetra-α-methylbiphenylene, tetra-β-methylbiphenylene, and octamethylbiphenylene, and the radical cation of octa-β-methyltetraphenylene have been generated and their ESR spectra have been recorded and analysed. In trifluoroacetic acid containing mercury(II) trifluoroacetate, the tetra-α-methylbiphenylene radical cation undergoes mono- and dimercuriation. Tetra-β-methylbiphenylene in tetrahydrofuran in the presence of lithium apparently undergoes ring-opening to give a radical anion derived from 2,2′-dilithiobiphenyl. The structures which these spectra imply, particularly the apparent distortion which has been reported in the tetraphenylene radical anion, are discussed.

Derivatives of biphenylene (**1**) and tetraphenylene (**2**) have an important place in radical ion and di-ion chemistry. Biphenylene readily undergoes oxidation and reduction to show strong, simple, persistent ESR spectra of the radical cation and anion, and this provided early support for the pairing theorem.[1] Hart has used the broadening of NMR signals which results from electron exchange between radical ion and substrate to show the formation of the radical cations of methylated biphenylenes in the presence of acids.[2] We have found that the biphenylene radical cation provides the best example of the mercuride-protonation reaction which occurs with some arenes in trifluoroacetic acid (TFAH) containing mercury(II) trifluoroacetate.[3]



(**1**) **a**; R = R′ = H
b; R = Me, R′ = H
c; R = H, R′ = Me
d; R = R′ = Me



(**2**) **a**; R = R′ = H
b; R = Me, R′ = H
c; R = H, R′ = Me
d; R = R′ = Me

Solutions of biphenylene and the methylated biphenylenes in superacids yield the dications which can be detected by ^{1}H and ^{13}C NMR spectroscopy,[4] and similarly reduction with lithium yields the dianions[5,6] which may then undergo ring opening to give 2,2′-dilithiobiphenyls.

Much less work has been carried out on the tetraphenylenes which are less readily available than the biphenylenes, but the molecular structure of the dianion is thought to be different from that of the neutral molecule.[7] Huber has shown that two radicals with different ESR spectra can be obtained from biphenylene, and has suggested that these two species again have different structures.[8,9]

Some of these points are discussed in more detail below.

Against this background we have carried out an ESR study of the radical cations and anions obtained from tetra-α-methyl-, tetra-β-methyl-, and octamethyl-biphenylene, the radical cation of tetraphenylene, and the radical cation of the new octa-β-methyltetraphenylene. Details of the spectra which have been observed are given in the Table.

Results

1,4,5,8-*Tetramethylbiphenylene* (**1b**).—The best spectra of the tetra-α-methylbiphenylene radical cation (**1b**)$^{+\bullet}$ were obtained from the light red solutions which (**1b**) forms in TFAH containing thallium(III) trifluoroacetate, without photolysis (Figure 1); the spectra were rapidly lost if the sample was irradiated. The spectrum appears as a 1:4:6:4:1 quintet due to coupling to the 4β-protons (see the Table), and any coupling to the 12 protons of the α-methyl groups was lost in the line width of *ca.* 0.15 G.

Three of the four possible ^{13}C satellites could be observed. As hyperfine coupling to the protons of the methyl groups is probably less than 0.02 G, the spin density at Cα is probably less than 0.001. In the ethyl radical where the spin density on Cα is unity, $a(^{13}\text{C}\beta)$ is *ca.* 13 G. Thus in (**1b**)$^{+\bullet}$, hyperfine coupling to the carbon of the methyl groups would be expected to be not greater than *ca.* 0.01 G, and this would be within the line width. We therefore tentatively assign the ^{13}C coupling constants of 3.04, 2.35, and 2.25 G to the α, β, and γ ^{13}C atoms respectively, on the same grounds as we used in discussing the biphenylene radical cation (**1a**)$^{+\bullet}$,[3] where the corresponding values are 3.21, 2.55, and 2.39 G.[12]

We could see no evidence for the formation of a dimer radical cation (**1b**)$_2^{+\bullet}$ equivalent to the familiar (**1a**)$_2^{+\bullet}$; the methyl groups probably sterically prevent the close approach of the two molecules. Compound (**1b**) in chloroform containing TFAH has been reported to give a broad ESR spectrum (ΔH_{pp} 8 G) which showed some splitting at −70 °C.[2]

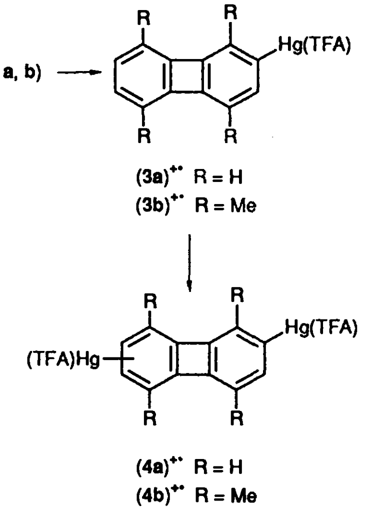
When (**1b**) was dissolved in TFAH containing mercury(II) trifluoroacetate it showed the same quintet spectrum of (**1b**)$^{+\bullet}$. When this sample was irradiated with UV light which was attenuated to 10% of its intensity by a neutral filter and passed through Pyrex glass, the spectral intensity was enhanced and mercuridеprotonation occurred (Scheme 1).

Figure 1(*b*) shows the spectrum after 10 min. The initial quintet (*g* 2.0025) has been largely transformed into a quartet

Table. ESR spectra of radical cations and anions of biphenylenes and tetraphenylenes.

Radical ion	H_α	H_β[a]/G	Others	g	Solvent[a]	T/K	Ref.
(1a)$^{+\cdot}$	0.21 (4 H)	3.58 (4 H)	3.21, 2.55, 2.39 (^{13}C)	2.0025	TFAH	262	12
(1a)$^{-\cdot}$	0.21 (4 H)	2.86 (4 H)	2.86, 2.44 (^{13}C)				
(3a)$^{+\cdot}$	0.21 (4 H)	3.58 (3 H)	76.5 (^{199}Hg)	2.0014	TFAH	262	3
(4a)$^{+\cdot}$	0.21 (4 H)	3.58 (2 H)		2.0007	TFAH	262	3
(1b)$^{+\cdot}$	<0.01 (12 H)	3.25 (4 H)	3.04, 2.35, 2.25 (^{13}C)	2.0025	TFAH	260	*b*
(1b)$^{-\cdot}$	0.18 (12 H)	2.75 (4 H)	3.65 (^{13}C)	2.0011	THF	243	*b*
(1b)$^{-\cdot}$			(^{7}Li)	2.0011	THF	243	*b*
(1b)$^{-\cdot}$			(^{39}K)	2.0011	THF	243	*b*
(3b)$^{+\cdot}$	<0.01 (12 H)	3.27 (3 H)	70.25 (^{199}Hg)	2.0014	TFAH	261	*b*
(4b)$^{+\cdot}$	<0.01 (12 H)	3.23 (2 H)	70.95 (^{199}Hg)	2.0004	TFAH	261	*b*
(1c)$^{+\cdot}$	0.08 (4 H)	4.70 (12 H)	3.5, 3.25 (^{13}C)	2.0024	TFAH	261	*b*
(1c)$^{-\cdot}$		3.72 (12 H)		2.00[c]	THF	243	*b*
(1d)$^{+\cdot}$	0.17 (12 H)	4.50 (12 H)		2.0026	TFAH	261	12
(1d)$^{+\cdot}$	0.33 (12 H)	3.04 (12 H)		2.0027	THF	243	*b*
(2a)$^{+\cdot}$	<0.01 (8 H)	1.34 (8 H)		2.0025	TFAH	260	*b*
(2a)$^{-\cdot}$	0.16 (8 H)	1.31 (8 H)			THF	183	*b*
(2a)$^{-\cdot}$	0.14 (4 H) 0.22 (4 H)	1.71 (4 H) 0.8 (4 H)			MeTHF		9
(2c)$^{+\cdot}$	0.19 (8 H)	2.15 (24 H)		2.0029	TFAH	261	*b*

[a] MeTHF = methyltetrahydrofuran. [b] Present work. [c] There is some doubt over the identification of the central line.



Scheme 1.

(g 2.0014). The reduction in the g-value causes the quartet to be superimposed at an intermediate stage on the upfield four lines of the initial quintet. Mercury contains a natural abundance of 16.84% ^{199}Hg, I 1/2, and ^{199}Hg satellites can be observed which reflect the quartet character of the central signal. Further photolysis reduces the central feature to a triplet (g 2.0007), with triplet primary ^{199}Hg satellites, and secondary satellites [Figure 1(*c*)] appear. Spectroscopic data are given in the Table, together with those for the monomercury and the dimercury derivatives of biphenylene itself for comparison.[3]

We assign the quartet central spectrum and quartet satellites to the monomercuriated species (3)$^{+\cdot}$, and the triplet central spectrum and triplet primary and secondary satellites to the dimercuriated species (4)$^{+\cdot}$ [Scheme 1] which probably comprises both the 2,6- and 2,7-dimercuriated isomers (see ref. 3). These two mercuriation steps appear to be faster than those in biphenylene itself (**1a**) to give the corresponding mono- and di-mercuriated derivatives,[3] but further reaction to give tri- and tetra-mercuriation is clearly slower with (**1b**) than with (**1a**), probably because of the steric congestion which develops.

When (**1b**) was treated with lithium in tetrahydrofuran (THF), the solution developed a light blue then a brown colour, and the spectrum of the radical anion as shown in Figure 2 was observed. The hyperfine coupling constants are given in the Table. The McConnell constant for coupling to the aromatic protons is less than it is in the corresponding radical cation, as would be expected,[10] but a significant coupling to the methyl groups can be observed, and the complexity which this confers allowed only the largest ^{13}C coupling constant to be identified.

When the reduction was carried out with potassium at 243 K, counterion coupling at *ca.* 0.7 G could be observed, but a good simulation of the spectrum could not be obtained. Similarly the spectrum in Figure 2 under higher resolution showed a further small hyperfine coupling, presumably to the lithium counterion, but again the simulation was unsatisfactory.

Thermolysis of biphenylene (**1a**) at 400 °C gives tetraphenylene (**2a**) in almost quantitative yield,[11] but we were unable to isolate octa-α-methyltetraphenylene (**2b**) from the thermolysis of tetra-α-methylbiphenylene (**1b**).

2,3,6,7-*Tetramethylbiphenylene* (**1c**).—The ESR spectrum of the radical cation of tetra-β-methylbiphenylene (**1c**)$^{+\cdot}$ in trifluoroacetic acid containing thallium(III) trifluoroacetate is shown in Figure 3, and the spectral data are given in the Table. The solutions are light yellow in colour. Similar spectra were obtained in SO_2/FSO_3H, in trifluoroacetic acid containing mercury(II) trifluoroacetate, and in CH_2Cl_2 containing aluminium trichloride, but the quintet coupling by the four aromatic protons was less well resolved. The outer pair of ^{13}C satellites with a 3.5 G can be assigned to the α positions of the aromatic rings. The inner pair with a separation of 2.5 G appear to result from the overlap of two signals, which could arise from the β, γ, or methyl carbon atoms.

A solution of (**1c**) in chloroform containing trifluoroacetic acid at room temperature has been reported to give a broad signal, ΔH_{pp} 15 ± 1 G, which resolved into a seventeen-line spectrum at −60 °C, with a(H) 2 G,[2] but such a spectrum

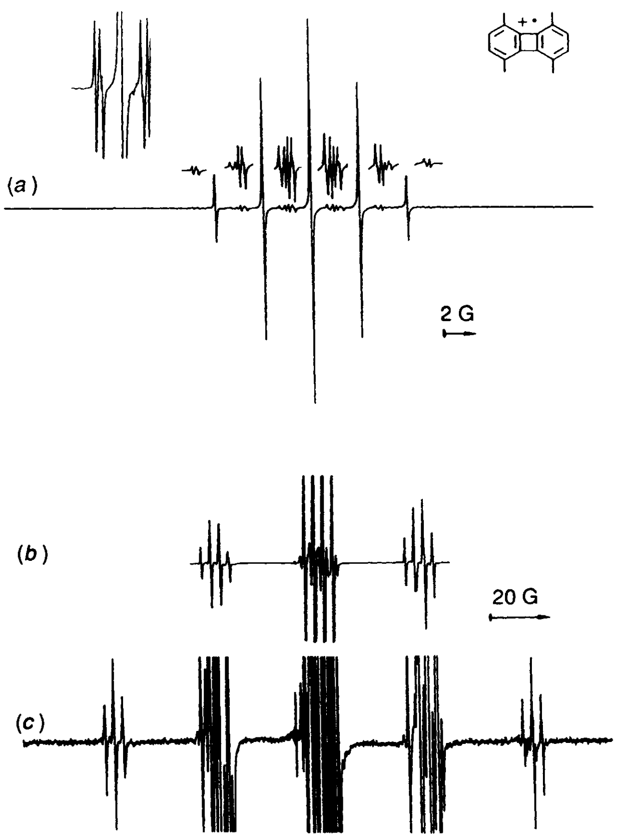


Figure 1. ESR spectra derived from (**1b**) in TFAH at −11 °C. (*a*) In the presence of $Tl(TFA)_3$ giving $(\mathbf{1b})^{+\bullet}$. The insets show the ^{13}C satellites at increased gain, and the ^{13}C satellites about the first line of the spectrum at increased gain and expansion. (*b*) In the presence of $Hg(TFA)_2$. The principal species present is the monomercuriated radical cation $(\mathbf{3})^{+\bullet}$; the central feature and the ^{199}Hg satellites are mainly quartets, with some triplet character due to the presence of some $(\mathbf{4})^{+\bullet}$. (*c*) In the presence of $Hg(TFA)_2$. Further mercuriation has occurred to give principally the dimercuriated species $(\mathbf{4})^{+\bullet}$; the secondary ^{199}Hg triplet satellites arise from molecules containing two ^{199}Hg atoms.

could relate to $(\mathbf{1c})^{+\bullet}$ only in the unlikely circumstance where hyperfine coupling by the protons at the α-positions and by the methyl groups at the β-positions were equal.

Treatment of (**1c**) in THF with potassium gave a solution which we believe to contain the dianion $(\mathbf{1c})^{2-}$. Photolysis of this gave the weak, short-lived spectrum of the radical anion $(\mathbf{1c})^{-\bullet}$ (Scheme 2) as shown in Figure 4.

When (**1c**) in THF was treated with lithium it gave a deep blue solution which showed only a complex spectrum which could not be analysed, and it is likely that our spectrum relates to a ring-opened species (see the Discussion). Thermolysis of tetra-β-methylbiphenylene (**1c**) at 400 °C gave the corresponding octa-β-methyltetraphenylene (**2c**), which was isolated in low yield as a crystalline solid; this compound has not been described previously.

2,3,4,5,7,8,9,10-Octamethylbiphenylene (**1d**).—In trifluoroacetic acid containing thallium trifluoroacetate, (**1d**) gives a deep blue solution which shows a strong spectrum of the radical cation $(\mathbf{1d})^{+\bullet}$ (see ref. 12 and the Table).

The radical anion was prepared by treating a solution of (**1d**) in THF with lithium at room temperature. The deep blue solution shows the ESR spectrum of $(\mathbf{1d})^{-\bullet}$ which is illustrated in Figure 5. Olah and Schleyer[6] found that the dianion showed

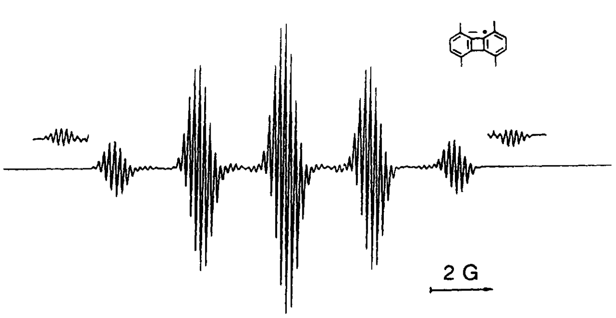


Figure 2. ESR spectrum of $(\mathbf{1b})^{-\bullet}Li^+$ in THF at −40 °C.

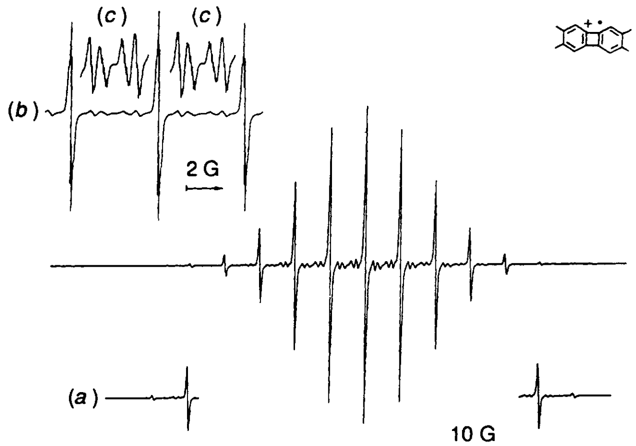


Figure 3. ESR spectrum of $(\mathbf{1c})^{+\bullet}$ in $TFAH/Hg(TFA)_2$ at −12 °C, showing inset (*a*) the wing lines of the 13-line multiplet, (*b*) the central lines with quintet coupling, and (*c*) the ^{13}C satellites about the central line.

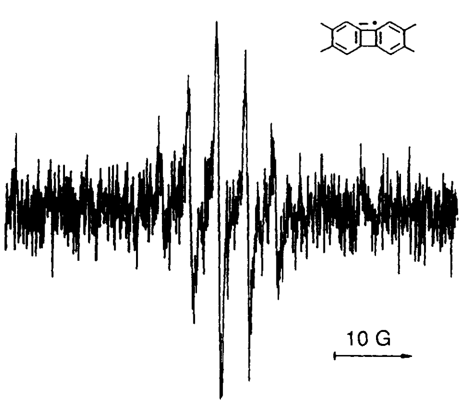


Figure 4. ESR spectra of $(\mathbf{1c})^{-\bullet}K^+$ in THF at −40 °C, from the photolysis of $(\mathbf{1c})^{2-}$.

two ^7Li NMR signals at room temperature, and at least *four* signals at −70 °C, and they suggested that this was to be ascribed to the formation of oligomeric aggregates. Our ESR spectra show no evidence of aggregation, and indeed we are not aware of this phenomenon having been observed with radical anions; however our concentrations of $(\mathbf{1d})^{-\bullet}Li^+$ are probably much lower than those of the $(\mathbf{1d})^{2-}2Li^+$ at which aggregation was observed.

Tetraphenylene (**2a**).—When a solution of tetraphenylene in trifluoroacetic acid containing mercury(II) trifluoroacetate was irradiated with UV light filtered through Pyrex glass, it showed the spectrum which is illustrated in Figure 6, which we ascribe to the radical cation $(\mathbf{2a})^{+\bullet}$. The spectrum shows hyperfine

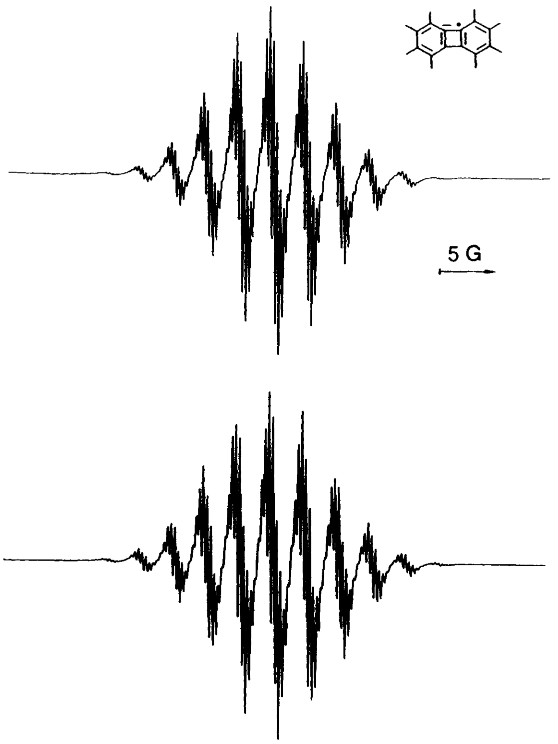


Figure 5. (*a*) ESR spectrum of $(\mathbf{1d})^{-\bullet}\mathrm{Li}^+$ in THF at −40 °C. (*b*) Computer simulation with the hyperfine coupling constants given in the Table, and a line width of 0.23 G.

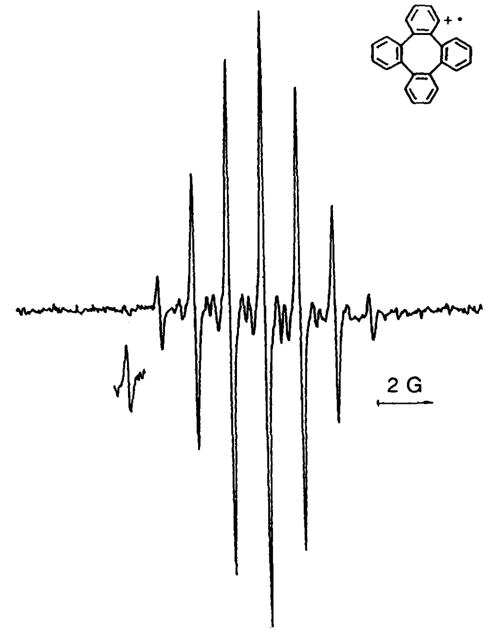


Figure 6. ESR spectrum of $(\mathbf{2a})^{+\bullet}$ in TFAF/Hg(TFA)$_2$ at −13 °C.

coupling of 1.34 G to eight equivalent protons in the β-positions, and coupling to the other eight protons was within the line width of 0.05 G.

The ESR spectrum of the radical anion of tetraphenylene has been described by Carrington *et al.*,[8] and by Huber.[9] By reduction with lithium in THF we obtained a strong, well resolved spectrum with hyperfine coupling constants similar to those reported previously (see the Table).

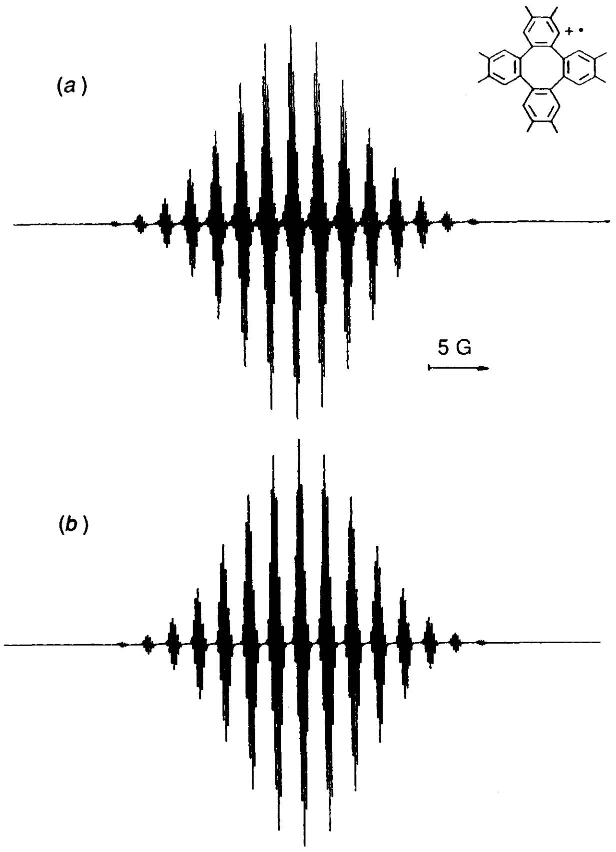


Figure 7. (*a*) ESR spectrum of $(\mathbf{2c})^{+\bullet}$ in TFAH/Hg(TFA)$_2$ at −12 °C. (*b*) Computer simulation using the hyperfine coupling constants given in the Table and a line width of 0.05 G, and ignoring ^{13}C coupling.

Octa-β-methyltetraphenylene (**2c**).—We were unable to observe any ESR spectrum when octa-β-methylbiphenylene in THF was treated with lithium or potassium with or without sonication in the absence or presence of 18-crown-6. However, treatment of (**2c**) in trifluoroacetic acid containing mercury(II) trifluoroacetate gave a light yellow solution which showed the strong spectrum of $(\mathbf{2c})^{+\bullet}$ which is illustrated in Figure 7. This simulates as a 25-plet of nonets; the ^{13}C hyperfine coupling could be observed but could not be analysed because of the small value of *a*(24 H), and the complication which results from the *a*(8 H) coupling.

Discussion

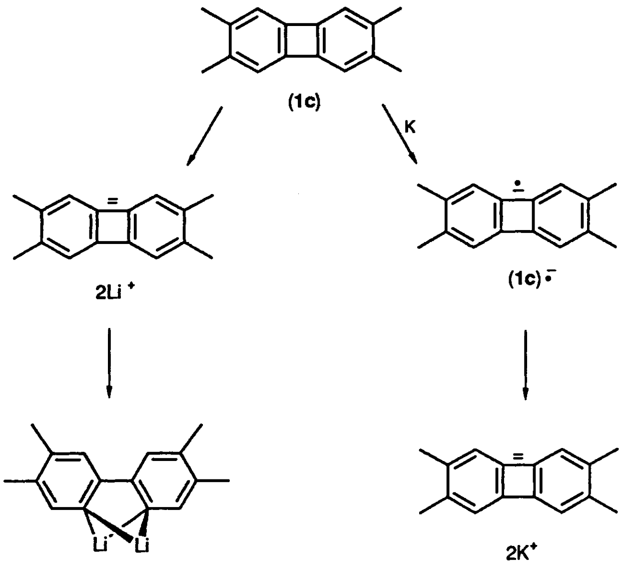
Biphenylenes.—The large hyperfine coupling to hydrogen or methyl at the β-positions, and the correspondingly small value at the α-positions, in both the radical cations and anions of the biphenylenes is in accord with the identical absolute values of the Hückel coefficients in the HOMO and LUMO of an alternant hydrocarbon. The hyperfine coupling at the β-positions in the radical cations is consistently greater than that in the same position in the corresponding radical anions; this is usual, and is ascribed to the effect of the positive charge in causing the 2p orbitals to contract.[13]

This positive charge effect is less obvious at the α-positions, where the coupling constants are at most 0.33 G and are sometimes undetectably small. However, the spin density at the α-positions in the different biphenylenes may vary in sign: Hart's[2] work shows that these signs could be obtained from the NMR spectra, but the directions of the contact chemical shifts of the relevant protons were not quoted.

Mercuriation.—The progressive mercurideprotonation which occurs in the β-position of the biphenylene radical cation has been discussed previously.[3] Monomercuriation and dimercuriation appear to occur more rapidly with (**1b**) than with (**1a**), and it was difficult to obtain a clean ESR spectrum of monomercuriated $(\mathbf{1b})^{+\bullet}$, uncontaminated by the spectrum of any dimercuriated species. Thereafter, further mercuriation of (**1b**) is apparently slower than that of (**1a**), probably because of the steric hindrance provided by the methyl substituents.

We have observed previously[14] that in a series of aromatic hydrocarbons, mercuriation occurs preferentially at the position of highest spin density, and that the ratio $a(^{199}\mathrm{Hg})/a(^{1}\mathrm{H})$ for the groups involved in the substitution is *ca.* 20.6. For the mono- and di-mercuriation of (**1b**), this ratio is 21.6 and 21.7 respectively, within the range of values previously observed. The significance of this constant ratio is discussed in ref. 4.

Lithiation.—The reactions by which the radical cations were prepared are standard processes, and require no further comment. Similarly most of the radical anions were generated by the usual technique of one-electron transfer from an alkali metal to the biphenylene. The exception was tetra-β-methylbiphenylene (**1c**) where this technique gave rise to a complicated spectrum, consisting of 13 or 15 groups of multiplets separated by about 2.8 G. One hyperfine coupling constant appeared to have the value of 5.87 G, but the spectrum may refer to more than one radical anion, and we have not been able to analyse it. Olah and Schleyer[6] have shown that (**1c**) is particularly sensitive to undergoing ring opening to give 2,2′-dilithiobiphenyl when it is treated with lithium (Scheme 2) and this reaction is probably the cause of the complication which we observe, though the exact nature of the radical anion formed is not clear.

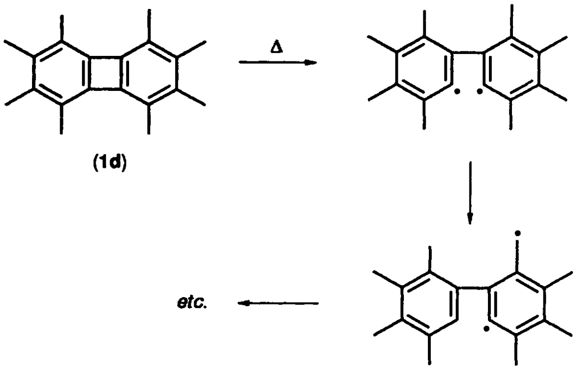


Scheme 2.

The only way in which we could obtain the weak spectrum of $(\mathbf{1c})^{-\bullet}$ as shown in Figure 4, was by photolysis of the brown solution which was formed when (**1c**) was treated with potassium. Presumably the reaction involves photoejection of an electron from the dianion $(\mathbf{1c})^{2-}$; we have observed a similar reaction previously for the dianions of pentalene[15] and fulvalene,[16] and Huber[9] has reported the equivalent reaction for the dianions of fluorene and of tetraphenylene.

$$(\mathbf{1c})^{2-}2\mathrm{M}^{+} \longrightarrow (\mathbf{1c})^{-\bullet} + \mathrm{M}^{+} + \mathrm{M} \qquad (1)$$

Tetraphenylenes.—Tetraphenylene (**2a**) is formed in excellent yield by the thermolysis of biphenylene (**1a**) at 400 °C.[11] When this reaction was carried out with the methylated biphenylenes (**1b**), (**1c**), and (**1d**), the mass spectra of the crude products showed that the corresponding tetraphenylenes were formed in very small yield, and from the reaction of tetra-β-methylbiphenylene (**1c**), the previously unknown octa-β-methyltetraphenylene (**2c**) was isolated by HPLC in about 6% yield. The reaction of biphenylene (**1a**) has been suggested to proceed through the formation of a ring-opened diradical, and when α-methyl groups are present, inter- and/or intra-molecular hydrogen transfer (Scheme 3) may detract from the yield of the tetraphenylene.



Scheme 3.

The central (cyclo-octatetraene) ring of tetraphenylene is non-planar, but a qualitative picture of the electron distribution can be obtained by the perturbation approach as used by Carrington *et al.*[8]

Figure 8 shows the electron distribution in the degenerate symmetric and antisymmetric bonding (ψ_{A1} and ψ_{S1}) and antibonding (ψ_{A2} and ψ_{S2}) orbitals of a benzene ring.

If tetraphenylene is considered to be built up from pair-wise interactions of benzene rings with a small overlap integral, the interaction between the ψ_{A} orbitals will be greater than that between the ψ_{S} orbitals because of the larger coefficients at what will be the α-positions in the tetraphenylene. This is illustrated in the perturbation diagram (Figure 8), which identifies the HOMO of the tetraphenylene radical cation $(\mathbf{2})^{+\bullet}$ as an antibonding combination of antisymmetric (ψ_{A1}) orbitals, and the SOMO of the radical anion $(\mathbf{2})^{-\bullet}$ as a bonding combination of antisymmetric (ψ_{A2}) orbitals. In both $(\mathbf{2})^{+\bullet}$ and $(\mathbf{2})^{-\bullet}$, this model predicts a large electron density at the eight β-positions, and a near-zero electron density at the eight α-positions.

This was the basis of the argument on which the spectrum of $(\mathbf{2a})^{-\bullet}$ was analysed.[8] We similarly assign the hyperfine coupling in $(\mathbf{2a})^{+\bullet}$ of a(8H) 1.35 G to the protons in the β-positions. It is interesting that this is slightly *less* than the corresponding value of 1.39 G in $(\mathbf{2a})^{-\bullet}$. We are not aware of any other example of an alternant hydrocarbon in which the positive charge does not have the reverse of this effect, but we note that if $(\mathbf{2a})^{+\bullet}$ and $(\mathbf{2a})^{-\bullet}$ remain non-planar like (**2a**), they cannot legitimately be considered as alternant hydrocarbons, and that there are other complications associated with the spectra of these species, as discussed below.

The spectrum of the radical cation of octa-β-methyltetraphenylene $(\mathbf{2c})^{+\bullet}$ which shows a large hyperfine 25-plet coupling to the β-methyl groups and a small nonet coupling to the α-hydrogen atoms confirms this predicted electron distribution.

We were unable to detect the spectrum of the radical anion $(\mathbf{2c})^{-\bullet}$ when (**2c**) was treated with lithium or potassium, with or without sonication. This can be rationalised on the grounds

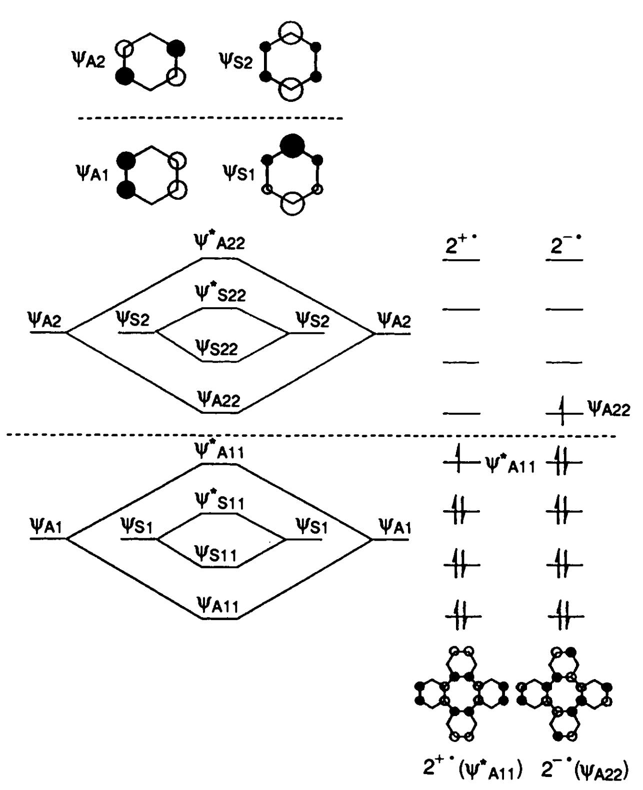


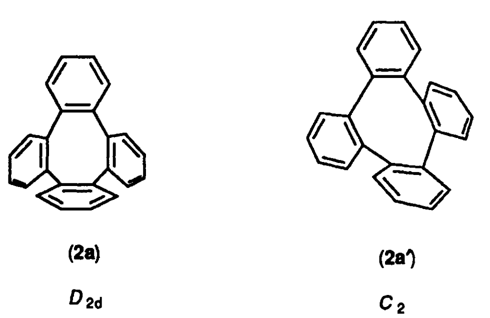
Figure 8.

that, if interaction between the benzene rings is small, each ring can be regarded as being analogous to durene for which we have been similarly unable to observe the formation of a radical anion, probably because electron repulsion by the methyl groups destabilises the radical anion.

These results can be compared with the very interesting work which has been carried out by Huber on the tetraphenylene radical anion (**2a**)$^{-\bullet}$ and dianion (**2a**)$^{2-}$.[9] X-Ray crystallography shows that tetraphenylene (and its inclusion complexes) is crown shaped with D_{2d} symmetry (as is cyclo-octatetraene which constitutes the central ring), and this is consistent with the fact that it shows only two ^{1}H and three ^{13}C NMR signals in solution. One-electron reduction gives the radical anion (**2a**)$^{-\bullet}$ with a(8H) 0.20 and 1.39 G, consistent with the same D_{2d} symmetry, but further reduction gives a dianion (**2a'**)$^{2-}$ which shows not two but *eight* ^{1}H NMR signals, and not three but *twelve* ^{13}C NMR signals. Photolysis of this dianion now generates a new radical anion (**2a'**)$^{-\bullet}$ with an ESR spectrum which is more complicated than that of (**2a**)$^{-\bullet}$, and which shows a(4H) 1.71, 0.87, 0.22, and 0.14 G.

Huber proposed that whereas (**2a**) has D_{2d} symmetry, (**2a'**)$^{+\bullet}$ has only C_2 symmetry, and that the radical anions (**2a**)$^{-\bullet}$ and (**2a'**)$^{-\bullet}$ retain the conformations of their closed shell precursors. Thus (**2a'**)$^{2-}$ and (**2a'**)$^{-\bullet}$ can be described as being comprised of two near-planar biphenyl units which themselves are near-orthogonal, and in (**2a'**)$^{-\bullet}$ the unpaired electron is concentrated in one biphenyl moiety. These structures are illustrated in Figure 9.

A similar effect might be looked for in the radical cation (**2a**)$^{+\bullet}$ as one-electron oxidation, like one-electron reduction, should strengthen the interaction between pairs of rings. We can see no sign of deviation from D_{2d} symmetry in the tetraphenylene or octamethyltetraphenylene radical cations (**2a**)$^{+\bullet}$ or (**2c**)$^{+\bullet}$. It is unfortunate that we were not able to generate the octa-β-methyltetraphenylene radical anion and dianion (**2c**)$^{-\bullet}$ and (**2c**)$^{2-}$, so these could be investigated for a similar effect. It would also be interesting to attempt to generate the tetraphenylene radical cation from the dication, and study these species in a similar way.


(**2a**) D_{2d}

(**2a'**) C_2

Figure 9.

The tetraphenylene structure is quite rigid, and it seems surprising that it could exist in a second conformation separated from the first by a barrier which (in the dianion) prevents interconversion at 150 °C. Further, we know of no other radical ion where the electron density is unsymmetrically distributed over a symmetric structure. We have considered the alternative possibility that the reduced symmetry in (**2a'**)$^{-\bullet}$ and (**2a'**)$^{2-}$ might be the result of a specific interaction with the counteranion [although no hyperfine coupling to the metal cation is apparent in the ESR spectrum of (**2a'**)$^{-\bullet}$].

We have used the MNDO method in an attempt to locate an energy minimum in which the radical anion or dianion of (**2a**) interacts with a lithium cation, but no such minimum could be found. Similarly the more recent AM1 and PM3 methods were unsuccessful in identifying a minimum using lithium or the appropriate 'sparkle' as the counterion.* The AM1 method showed that the D_{2d} structure (Figure 9) represents a minimum in the energy of both the radical anion and the dianion, but we cannot exclude the possibility that the C_2 structure might represent a deeper minimum.

Experimental

1,4,5,8-Tetramethylbiphenylene (**1b**).—2,3-Dibromo-*p*-xylene[18] (8.0 g, 30 mmol) in dry THF (455 cm^3) was treated at −78 °C with butyl-lithium (60.6 mmol) in hexane. The mixture was stirred for 2 h, then warmed to room temperature. Hydrolysis yielded 1,4,5,8-tetramethylbiphenylene which was recrystallised from methanol–dichloromethane as pale yellow crystals (0.17 g, 5.5%), m.p. 227 °C (lit.,[2] 228.5–229 °C). $\delta_H(CCl_4)$ 2.12 (12 H, s, Me), and 6.25 (4 H, s, ArH).

2,3,6,7-Tetramethylbiphenylene (**1c**).—4-Bromo-*o*-xylene was iodinated in the presence of nitrosylsulphuric acid (from sulphur dioxide and fuming nitric acid[19]) to give 4-bromo-5-iodo-*o*-xylene, m.p. 66.5 °C.[20]

This dibromide (9 g) in ether (50 cm^3) was added during 30 min to a stirred suspension of magnesium (1.1 g) in ether (50 cm^3) under nitrogen. The mixture was stirred for a further 2 h then left to stand for two days. The solution was hydrolysed with aqueous ammonium chloride, to yield pale yellow crystals (from ethanol; 0.12 g), m.p. 219 °C (lit.,[21] 224–224 °C). $\delta_H(CCl_4)$ 2.02 (12 H, s, Me) and 6.40 (4 H, s, ArH).

Tetraphenylene (**2a**).[11]— Biphenylene (0.1 g) was pyrolysed in an evacuated sealed Pyrex tube for 1 h at 400 °C. The product was purified by chromatography on silica gel, but on oxidation

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* A 'sparkle' is an ion of diameter 1.4 Å, with the charge distributed over its surface.[17]

it still showed the ESR spectrum of the biphenylene radical cation. It was therefore further purified by preparative HPLC on a 50 × 250 × 4.6 mm column of Nucleosil 5 m silica gel with a mobile phase of CH_2Cl_2–light petroleum (3:97) and a flow rate of 1.5 cm^3 min^{-1}. Tetraphenylene was obtained as white crystals, m.p. 210 °C, *m/z* 304 (Calc. for $C_{24}H_{16}$: 304).

2,3,6,7,10,11,14,15-*Octamethyltetraphenylene* (**2c**).—2,3,6,7-Tetramethylbiphenylene[12] (0.1 g) was sealed in a Pyrex tube under vacuum and heated at 400 °C for 1 h. Mass spectrometry showed the presence of the tetraphenylene (*m/z* 416), and this was isolated by HPLC as a white solid (12 mg, 6%), m.p. >290 °C. $\delta_H(CDCl_3)$ 2.20 (24 H, s, Me) and 6.90 (8 H, s, ArH). $\delta_C(CDCl_3)$ 19.40 (Me), 130.75, 135.00, and 139.25 (Ar); *m/z* (70 eV) 417 (42.5%), 416 (100; M^+), 386 (15.8), 193 (18.7), 186 (10.9), 178 (15.3), and 170 (10.8) (Found: C, 92.45; H, 7.5. $C_{32}H_{32}$ requires C, 92.96; H, 7.74%).

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16-*Hexadecamethyltetraphenylene* (**2d**).—Pyrolysis of octamethylbiphenylene under similar conditions gave a dark brown oil. The mass spectrum showed that a small amount of the tetraphenylene (*m/z* 528) was present, but we were unable to isolate it by HPLC.

ESR Spectroscopy.—ESR spectra were recorded using a Varian E109 or Bruker ESP300 instrument, fitted with a 500 W high pressure mercury lamp provided with neutral (metal gauze) and glass filters, focused on the cavity. To prepare the radical anions, the degassed solution of the substrate in THF in a sealed silica tube was brought into contact with a potassium mirror or with a slice of lithium which was in contact with a chip of silica to abrade the surface. If the reduction was slow, it accelerated by immersing the tube in an ultrasonic cleaning bath.

MO Calculations.—Calculations were carried out on a Vax 6310 computer using the MOPAC 5 programs.

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