An Electron Spin Resonance Study of the Formation of Radical Cations in FSO_3H/SO_2 Solution

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Arenes which in FSO_3H/SO_2 solution show the n.m.r. spectra of the carbocations resulting from proton addition, also show the e.s.r. spectra of the radical cations resulting from electron loss. This provides a convenient technique for studying the e.s.r. spectra of radical cations in fluid solution down to *ca.* 180 K.

A few compounds show special behaviour. 2,3-Dihydrophenylene and acenaphthene give rise to spectra which show that protons have been replaced, and which have a high *g* value. It is proposed that this results from the introduction of a disulphide bridge across the *peri* positions. Stilbene and diphenylacetylene show spectra with 'normal' *g* values, but which are different from the spectra previously ascribed to the corresponding radical cations, and which appear to imply that there are non-equivalent *ortho* protons.

There is much current interest in experimental and theoretical aspects of radical cation chemistry.[1] A number of new techniques have been developed for observing the e.s.r. spectra of these species in fluid solution, and the reagents now available include H_2SO_4,[2] CF_3CO_2H or $C_3F_7CO_2H$,[3] CCl_3CO_2H,[4] CF_3SO_3H,[5] FSO_3H,[6] FSO_3H/SO_2ClF,[7] $Hg(OCOCF_3)_2$,[8] $Tl(OCOCF_3)_3$,[9] Pb^{IV},[10] $AlCl_3$,[11] BF_3,[12] $SbCl_3$,[13] $SbCl_5$,[14] $Co(OCOCF_3)_3$,[15] Ag^+,[16] $SO_4^{-\bullet}$,[17] and triarylaminium radical cations.[18] In most cases, the electron transfer may be photo-assisted. Rather limited use has also been made of electrolytic oxidation.[19]

Despite this variety of techniques, there is still a need for better methods: indeed the very variety indicates the limitations of the present procedures, and the continual search for improvements.

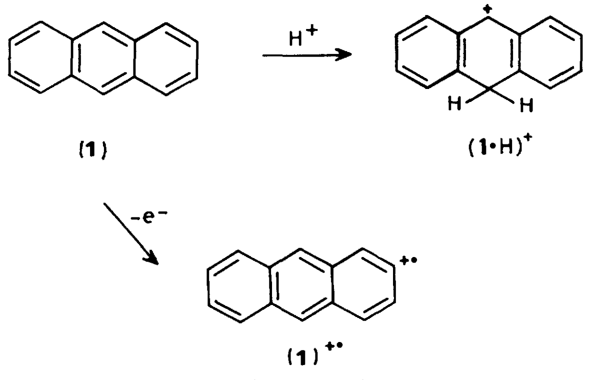
Sulphuric acid (m.p. 12 °C) and trifluoroacetic acid (m.p. −15 °C), which are in common use, have the disadvantage that they cannot be used at low temperatures, so that radical cations which are unstable near room temperature cannot be observed, and variable temperature studies cannot be carried out. Similar acid systems which could be used at much lower temperatures would be valuable.

A number of superacid solvents have been developed for use at low temperatures, particularly for investigating by n.m.r. spectroscopy the formation of carbocations,[20] and it seemed likely that some of these systems might also be suitable for the generation of radical cations. A few studies have been carried out using FSO_3H/SO_2ClF as the solvent for generating radical cations,[7] but no systematic study of any of these media has been carried out.

We report here an e.s.r. study of the formation of radical cations in a solvent consisting of liquid sulphur dioxide containing fluorosulphonic acid. This system remains liquid down to low temperatures and has been used extensively for n.m.r. studies.[21]

Results

A solution of anthracene (**1**) in a mixture of liquid sulphur dioxide and fluorosulphonic acid (1:1, v/v) at 193 K shows the ^1H n.m.r. spectrum [Figure 1(*a*)] of the anthracenium carbocation $(\mathbf{1}\cdot H)^+$.[20] Conversion to the carbocation is normally regarded as being complete for such substrates. However, the same solution shows an e.s.r. spectrum of the anthracene radical cation $(\mathbf{1})^{+\bullet}$ [Figure 1(*b*)], and quantitative measurements showed that in a 4×10^{-2} mol dm^{-3} solution *ca.* 4% of the anthracene was present as the radical cation. Thorough degassing of the solvent by repeated freeze–thaw cycles before it was mixed with the anthracene did not affect the intensity of the e.s.r. spectra.



(**1**) (**1**·H)$^+$ (**1**)$^{+\bullet}$

$$ArH + ArH_2^+ \longrightarrow ArH^{+\bullet} + ArH_2^\bullet$$

Strong e.s.r. spectra were also observed when the further compounds shown in the Table were dissolved in the same solvent. Some of the compounds showed the spectra of the radical cation as soon as the solutions were prepared at 270 K, but for others the spectra developed only when the solutions were warmed to 230 K or irradiated with u.v. light filtered through Pyrex glass at 230 K. Details are given in the Experimental section.

A number of different mechanisms have been considered to explain the formation of radical cations of arenes in strong acid solutions.[29] The participation of aerobic oxygen is invoked in some of these mechanisms, but in the case of anthracene we think we have excluded this possibility. In the absence of oxygen, the most reasonable mechanism would appear to be that in which the arene is oxidised by the protonated arene, as shown in equation (2).

Most of the radical cations in the Table have been reported before, and require no further comment.

The tetramethyl-1,4-dioxine radical cation $(\mathbf{11})^{+\bullet}$ was obtained by dissolving acetoin dimer in SO_2/FSO_3H at 190 K and warming the solution to 230 K. Russell *et al.* observed a similar

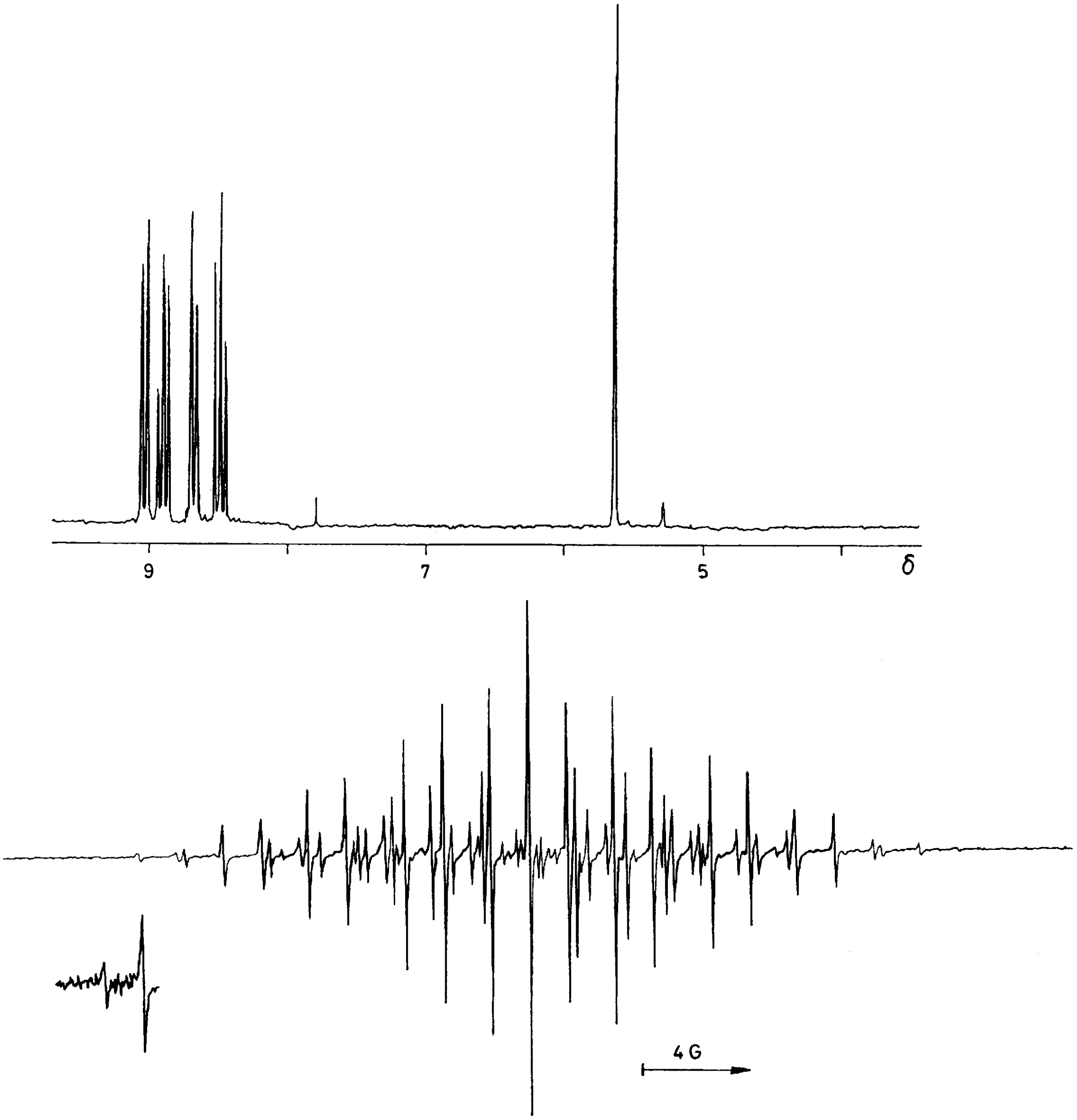


Figure 1. (*a*) ^{1}H N.m.r. spectrum of a solution of anthracene (**1**) in SO_2/FSO_3H at 193 K showing the formation of the carbocation $(\mathbf{1}\cdot H)^+$. (*b*) E.s.r. spectrum of the same solution showing the presence of the radical cation $(\mathbf{1})^{+\cdot}$.

dehydration–oxidation when acetoin dimer was dissolved in sulphuric acid.[28] Our spectrum is shown in Figure 2. The inset shows the ^{13}C satellites in the central region of the spectrum, and these can be simulated using the hyperfine coupling constants a(12 H) 4.04, $a(^{13}C$, 4 C) 2.45, and $a(^{13}C$, 4 C) 0.65 G. Russell *et al.* reported a(12 H) 4.06, $a(^{13}C)$ 2.3 G.

These two ^{13}C hyperfine coupling constants can be assigned to the ring and the methyl carbon atoms by making use of the principle that in a methylated π-radical, the ratio $a(^{13}C\beta)/a(H\beta)$ should be approximately constant. This is illustrated for the following radicals for which are given in sequence the values (G) for $a(^{13}C\beta)$, $a(H\beta)$, and $a(^{13}C\beta)/a(H\beta)$: CH_3CH_2 13.57, 26.87, 0.505; $(CH_3)_2CH$ 13.2, 24.74, 0.534; $(CH_3)_3C$ 12.35, 22.71, 0.544;[29] $(CH_3)_5C_5^{\cdot}$ 3.35, 6.4, 0.523;[30] and $(CH_3)_4C_4^{+\cdot}$ 4.04, 8.70, 0.46.[31] We conclude that $a(^{13}C\beta)$ should be approximately half $a(H\beta)$, and thus we assign the coupling constants in the tetramethyldioxine radical cation as $a(^{13}C\alpha)$ 0.65, $a(^{13}C\beta)$ 2.45 G.

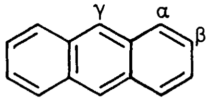
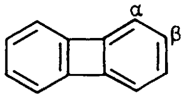
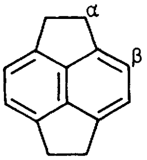
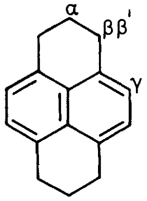
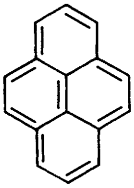
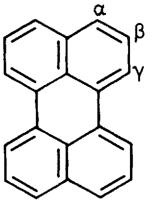
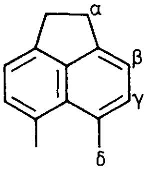
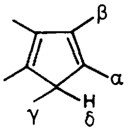
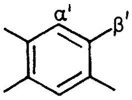
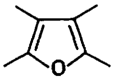
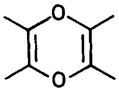
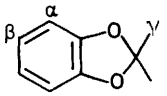
The spectrum of the radical cation of 2,2-dimethyl-4,5-benzo-1,3-dioxolane (**12**) has not been observed before, but Dixon and Murphy[32] obtained the spectrum of the radical cation of benzodioxolane itself using a flow system with Ce^{IV} in concentrated sulphuric acid, and reported a(2 H) 0.4, a(2 H) 4.9, a(2 H) 21.9 G. We obtained the same spectrum of $(\mathbf{12})^{+\cdot}$ from (**12**) in SO_2/FSO_3H (see Table), and also by photolysis of a solution of (**12**) in dichloromethane in the presence of $AlCl_3$ at 193 K with u.v. light filtered through Pyrex glass.

The coupling constants and g values which are listed in the Table are close to the values in the literature: there appear to be no unusual medium effects. In general the spectra show narrow line-widths and good signal to noise ratios, the solvent is easy to handle, and the solutions stay liquid down to about 180 K.

A few compounds, however, showed special behaviour in the SO_2/FSO_3H solvent; we discuss here the behaviour of 2,3-dihydrophenylene, acenaphthene, stilbene, and diphenylacetylene.

2,3-Dihydrophenylene and Acenaphthene.—The e.s.r. spectrum of the radical cation of 2,3-dihydrophenylene (**13**) has not been reported previously. In SO_2/FSO_3H at 217 K it gave the spectrum shown in Figure 3(*a*), a(2 H) 11.31, a(2 H) 2.85, a(2 H) 3.86, a(4 H) 0.34 G, g 2.0079. The high g value and the loss of hyperfine coupling by two protons imply that two heteronuclear

Table. E.s.r. spectra of radical cations in FSO_3H/SO_2.[a]

	Compound	*a*/G		*g*	*T*/K	Ref.
(1)		3.09 (4 Hα) (3.08)	1.37 (4 Hβ) (1.38)		193	14
		6.59 (2 Hγ) (6.47)				
(2)		0.21 (4 Hα) (0.21)	3.55 (4 Hβ) (3.69)	2.0026	193	22
(3)		13.04 (8 Hα) (13.13)	2.04 (4 Hβ) (2.03)	2.0029	190	23
(4)		0.40 (4 Hα) (0.40)	14.63 (4 Hβ) (14.63)	2.0026	185	24
		3.90 (4 Hβ') (3.90)	1.90 (4 Hγ) (1.90)			25
(5)		1.2 (2 Hα) (1.18)	5.40 (2 Hβ) (5.38)		217	14
		2.12 (2Hγ) (2.12)				
(6)		4.05 (4 Hα) (4.04)	0.42 (4 Hβ) (0.44)		196	14
		3.05 (4 Hγ) (3.04)				
(7)		12.90 (4 Hα) (12.89)	2.50 (2 Hβ) (2.51)	2.0027	215	23
		1.42 (2 Hγ) (1.14)	8.62 (6 Hδ) (8.58)			
(8)		14.8 (6 Hα) (15.0)	4.0 (6 Hβ) (4.0)		243	3
		0.8 (3 Hγ) (0.8)	1.6 (1 Hδ) (1.6)			
(9)		0.77 (2 Hα') (0.78)	10.6 (6 Hβ') (10.59)		198	26
(10)		16.1 (6 Hα) (16.2)	3.8 (6 Hβ) (3.8)	2.0024 (2.0024)	193	27
(11)		4.04 (6 Hα) (4.06)		2.0043	131	28
(12)		0.4 (2 Hα)	4.9 (2 Hβ)		193	
		0.4 (6 Hγ)				

[a] Data from the literature are given in parentheses.

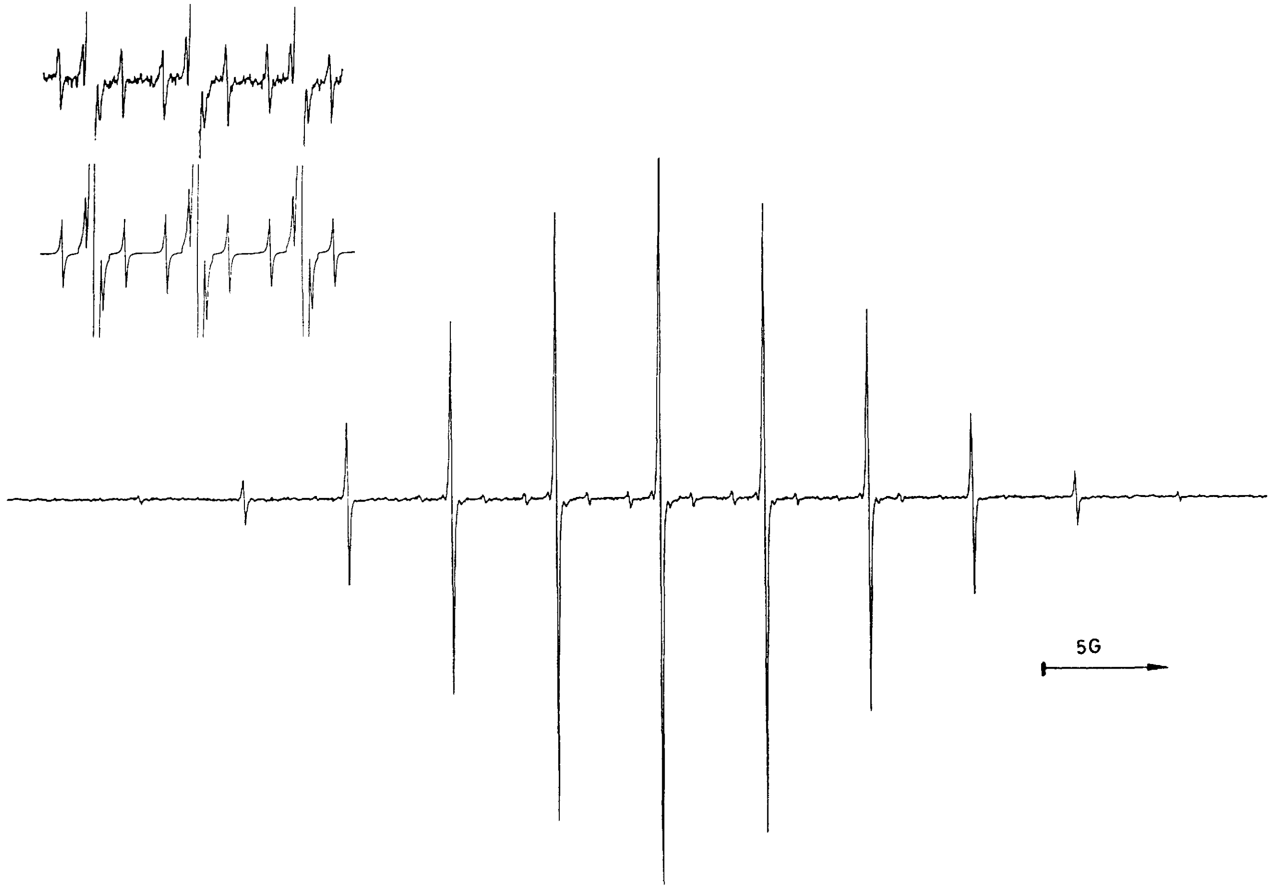
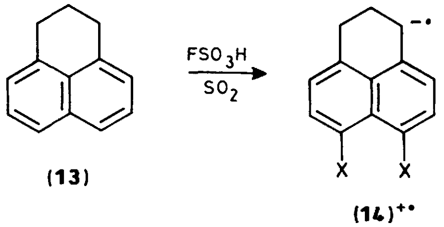


Figure 2. E.s.r. spectrum of the tetramethyldioxine radical cation $(\mathbf{11})^{+\cdot}$ in SO_2F/SO_3H at 230 K. The inset shows the ^{13}C satellites about the principal central three lines, and the simulation using the hyperfine coupling constants given in the text.

substituents have been introduced, and as this does not occur in compounds (**3**), (**4**), and (**7**) where the *peri* positions are blocked, we assume that this substitution occurs at the *peri* position to give $(\mathbf{14})^{+\cdot}$

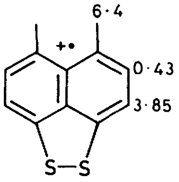


(**13**) $(\mathbf{14})^{+\cdot}$

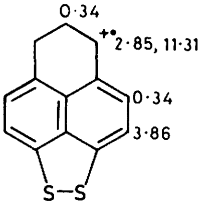
Attachment of the substituents through oxygen appears to be ruled out because the oxygen-substituted arenes usually have *g*-values between 2.0030 and 2.0040. For example the radical cation of 1,8-dihydroxynaphthalene has *g* 2.0030, and the highest value we have been able to find for such a compound is 2.0040 for 1,2,4,5-tetramethoxybenzene.[33]

Sulphonates and related compounds also seem to be excluded because of their high oxidation potentials,[34] and indeed we are not aware of the e.s.r. spectra of the radical cations of any sulphonates being observed in solution.

The most likely identity of the substituent X appears to be sulphur, probably as a disulphide bridge. Bakker, Claridge, and Kirk[34] showed that naphthalene and a variety of mono- and di-methylnaphthalenes in $AlCl_3/SO_2/CH_2Cl_2$ showed e.s.r. spectra with *g* 2.0079–2.0084 which were ascribed to the *peri*-disulphides. For example the hyperfine coupling constants which they observed for the radical cation from 1,8-dimethylnaphthalene are appended to the formula $(\mathbf{15})^{+\cdot}$, and those from our analysis of the spectrum which we obtain from dihydrophenalene are shown in $(\mathbf{16})^{+\cdot}$.



$(\mathbf{15})^{+\cdot}$



$(\mathbf{16})^{+\cdot}$

The spectrum of $(\mathbf{16})^{+\cdot}$ showed a strong alternating line width effect [Figure 3(*b*)] which can be ascribed to inversion of the six-membered ring which exchanges the pseudo-axial and pseudo-equatorial protons of the α-methylene groups with *a*(2 H) 11.31 and *a*(2 H) 2.85 G. A thorough study of the temperature dependence of the spectra was not carried out, but from simulation of the spectra at 255, 235, and 217 K, the activation energy to inversion was deduced to be *ca.* 36.4 ± 4 kJ mol^{-1}. For comparison, the equivalent inversion barriers have been found to be in the dihydrophenalene analogues (**13**) 35 kJ mol^{-1} [35] and $(\mathbf{13})^{-\cdot}$ 30 ± 0.7 kJ mol^{-1},[36] and in the hexahydropyrene analogues $(\mathbf{4})^{+\cdot}$ 32.2[37] and $(\mathbf{4})^{-\cdot}$ 29.9 kJ mol^{-1}.[38]

The behaviour of acenaphthene (**17**) can be interpreted in a similar way to that of dihydrophenalene (**13**). In molten

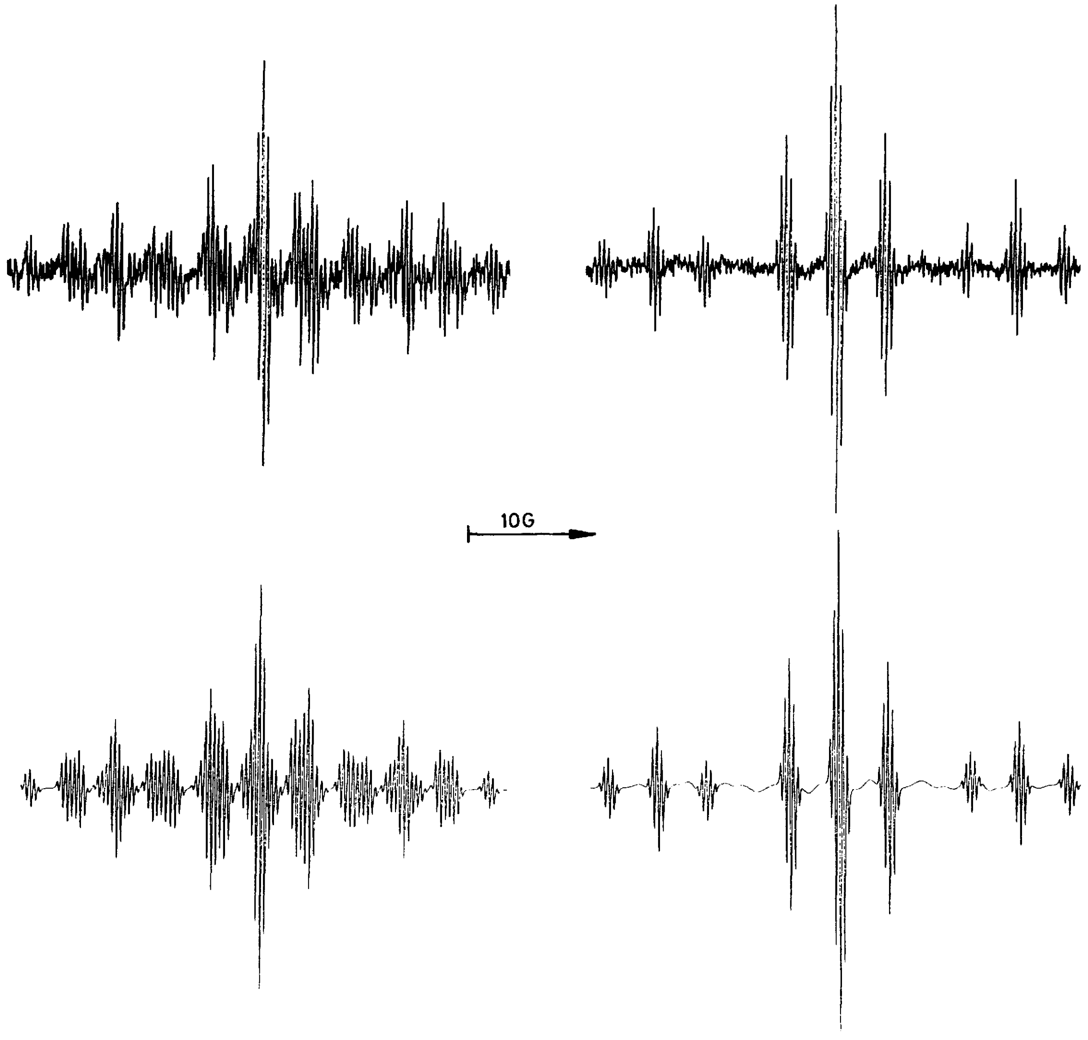
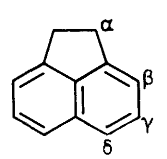


Figure 3. E.s.r. spectrum and simulation of the radical cation derived from 2,3-dihydrophenalene (**13**) in SO_2/FSO_3H at (*a*) 217 K and (*b*) 255 K.



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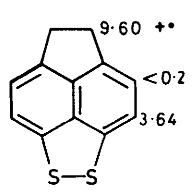
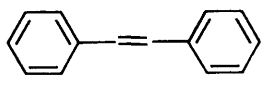


(18)$^{+\bullet}$



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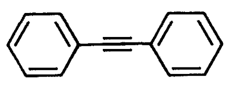


(20)

$SbCl_3/AlCl_3$ it shows a spectrum with a(4 Hα) 13.18, a(2 Hβ) 3.13, a(2 Hγ) 0.59, a(2 Hδ) 6.59 G, g 2.0027.[13]

In SO_2/FSO_3H it gives the spectrum illustrated in Figure 4, which consists of a simple quintet of triplets, a(4 H) 9.60, a(2 H) 3.64 G, g 2.0078. The same spectrum was obtained with SO_2/H_2SO_4 as the reagent. No spectrum was observed with (**17**) in SO_2ClF/FSO_3H, but when SO_2 was bubbled through the solution, the same spectrum shown in Figure 4 was obtained.

The high g value again would be consistent with the formation of a disulphide, and for the reasons given above, we believed that this occurs across the *peri* positions as shown in (**18**)$^{+\bullet}$. We observed the formation of an analogous *peri*-dimercurated radical cation when acenaphthene was treated with $Hg(O_2CCF_3)_2/CF_3CO_2H$.[39] It appears likely that the product is the peridisulphide with the assignment of the hyperfine coupling constants (G) as shown in (**18**)$^{+\bullet}$, where the coupling to the hydrogen atoms at positions β is <0.2 G.

Stilbene and Diphenylacetylene.—It is less easy to interpret the results which we have obtained with these two compounds. Photolysis of a solution of (*Z*)- or (*E*)-stilbene (**19**) in trifluoroacetic acid containing mercury(II) trifluoroacetate at 261 K gave rise to a spectrum which we ascribed to the *E*-radical cation (**19**)$^{+\bullet}$, with a(2 H alkenic and 2*p*-H) 4.53, a (4*o*-H) 2.78, a(4*m*-H) 0.715 G, g 2.0026,[40] and in the present work we have duplicated this result at 233 K using CH_2Cl_2 as a cosolvent. These hyperfine coupling constants correlate satisfactorily with the values observed for (**19**)$^{-\bullet}$, and those calculated by Huckel theory,[40] and we have no reason to doubt the assignment of the spectrum to (**19**)$^{+\bullet}$. However, when a solution of (*E*)-stilbene in SO_2/FSO_3H was warmed to 233 K, the new spectrum shown in Figure 5 developed. The same spectrum was obtained with (*Z*)-stilbene and also with (*E*)-4,4′-di-t-butylstilbene; presumably

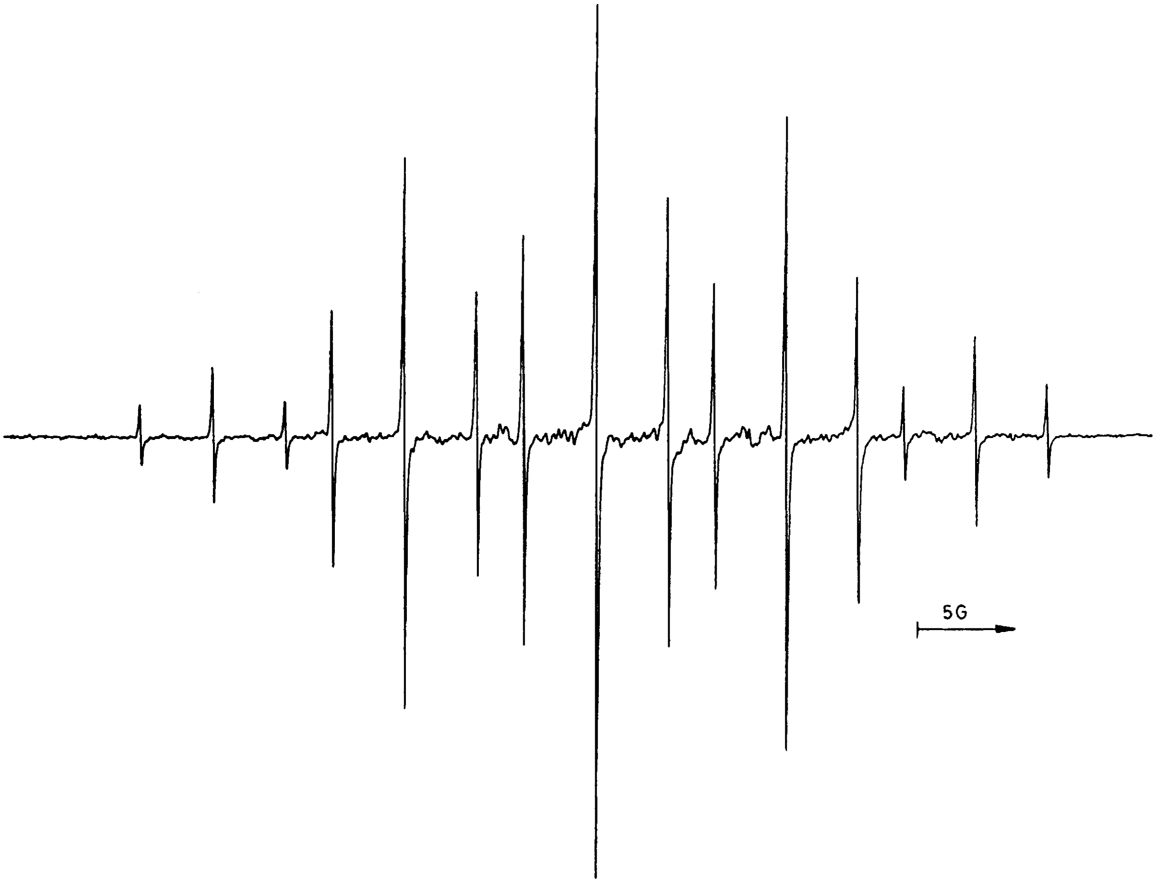


Figure 4. E.s.r. spectrum of the radical cation derived from acenaphthene (**17**) in SO_2/FSO_3H at 233 K.

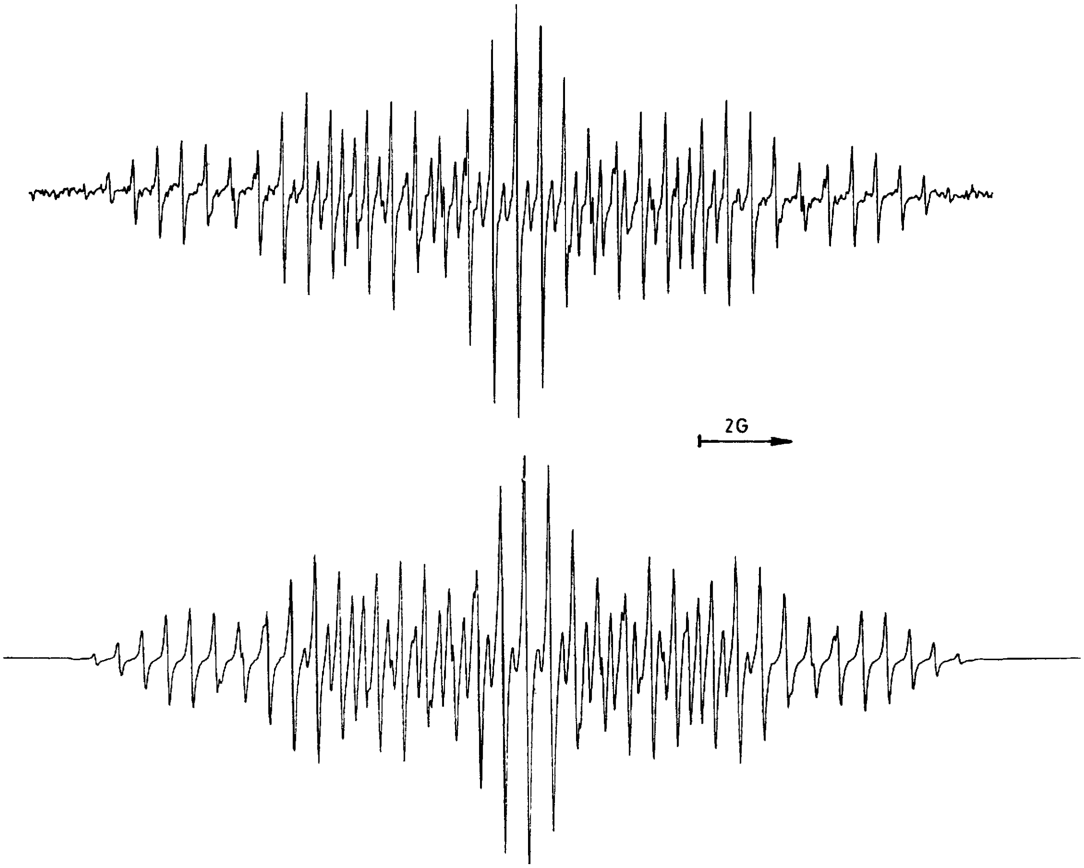


Figure 5. E.s.r. spectrum and simulation of a solution of stilbene (**19**) in SO_2/FSO_3H at 246 K.

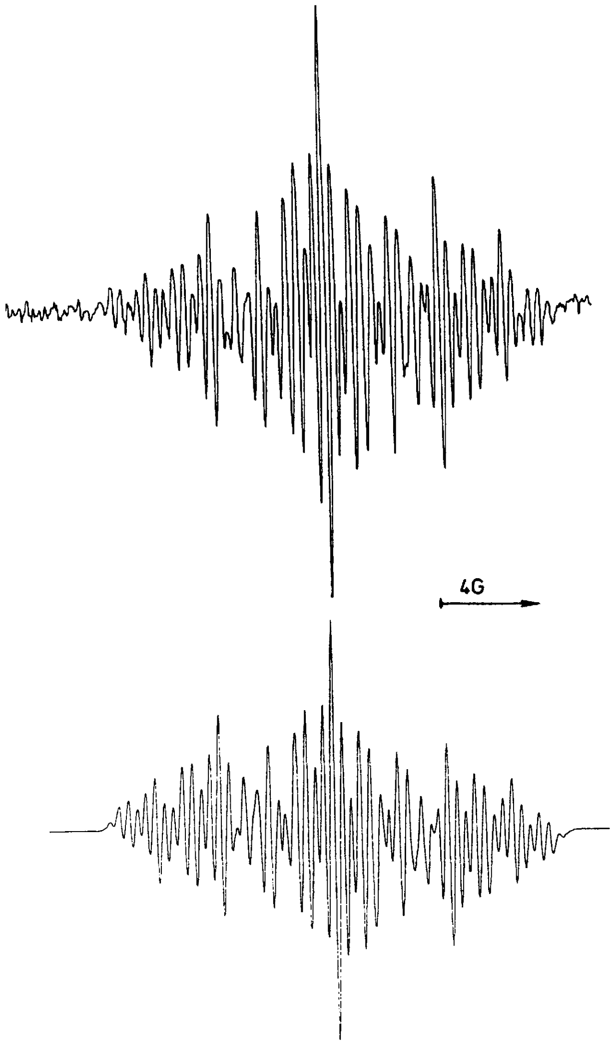


Figure 6. E.s.r. spectrum and simulation of a solution of diphenylacetylene (**20**) in SO_2/FSO_3H at 230 K.

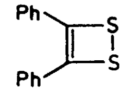
isomerisation of the *Z*-isomer occurs as it does in trifluoroacetic acid, and under the strong acid conditions the di-t-butylstilbene undergoes protodealkylation.

The spectrum can be simulated [Figure 5(*b*)] using the hyperfine coupling constants *a*(2 H) 4.69, *a*(2 H) 2.78, *a*(2 H) 1.09, *a*(6 H) 0.53 G, *g* 2.002 46. These are different from those which we observed in CF_3CO_2H solvent, and they present the further problem that they imply the absence of axial symmetry in the phenyl groups and the lack of rotation about the C–Ph bond.

A similar problem is encountered with diphenylacetylene. In trifluoroacetic acid it gives a weak but characteristic spectrum with *g* 2.0024, which could not be analysed convincingly.[41] When mercury(II) trifluoroacetate was added, the spectrum changed to that of the radical cation of 1,2,3-triphenylazulene, indicating dimerisation and ring expansion.[42]

With SO_2/FSO_3H as solvent we obtained the spectrum shown in Figure 6, *g* 2.0025, which could be simulated using the hyperfine coupling constants *a*(2 H) 4.55, *a*(2 H) 2.56, *a*(2 H) 1.06, and *a*(4 H) 0.38 G. This spectrum is different both from that which we obtained in CF_3CO_2H, and from that of the azulene radical cation which is formed in the presence of Hg^{II}. Again, to obtain a satisfactory simulation we have to assume the non-equivalence of the *ortho* protons in the benzene rings.

A general similarity between the hyperfine coupling constants and the *g*-values obtained for stilbene and diphenylacetylene (which may be simply fortuitous) is apparent. In both, the number of coupling protons suggests that the molecules are monomeric, and the 'normal' *g*-values might be taken to imply that they are hydrocarbons.



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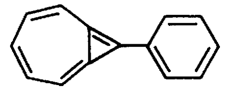

(22)

We have not been able to arrive at a convincing assignment of these spectra, but possibilities which we have considered include the following.

(*a*) Cyclisation could occur to give a phenanthrene derivative. Diphenylacetylene might be expected to give, after a hydrogen shift, phenanthrene itself, whereas stilbene would give a dihydrophenanthrene. We have previously obtained the e.s.r. spectrum of phenanthrene in trifluoroacetic acid [*a*(2 H) 4.91, *a*(4 H) 2.94 and 1.34 G, *g* 2.0024],[40] and it is different from the spectra of either diphenylacetylene or stilbene in SO_2/FSO_3H. With neither phenanthrene nor 9,10-dihydrophenanthrene in SO_2/FSO_3 at 233 K, could we observe an e.s.r. spectrum.

(*b*) The acetylenes may be forming diphenyldithiete (**21**), analogous to the epidisulphides which we believe are formed from acenaphthene and dihydrophenylene. The radical cation of diphenyldithiete $(\mathbf{21})^{+\bullet}$ has been obtained by Bock *et al.* by treating diphenylacetylene with S_2Cl_2 and $AlCl_3$ in CH_2Cl_2.[43] Hyperfine coupling to the phenyl groups could not be resolved, and in this and all the other phenyldithietes obtained, the *g* value was much higher (2.0144–2.0148) than we observe.

(*c*) The diphenyldiacetylene may be reacting to the stage of an intermediate [possibly (**22**)] which, it may be postulated, exists along the route to triphenylazulene.[42]

However, the observed coupling constants bear no clear relation to those calculated for $(\mathbf{22})^{+\bullet}$ by simple Hückel theory, and this model would not help to explain the apparently related behaviour of stilbene.

(*d*) The radical cations could relate to the chemically unchanged stilbene and diphenylacetylene, but strong association with the counter-ion FSO_3^- breaks the axial symmetry of the rings and perturbs the electron distribution. This seems unlikely: counter-ion interaction is not usually observed with radical cations, and none is apparent in any of the compounds $(\mathbf{1})^{+\bullet}$–$(\mathbf{12})^{+\bullet}$.

Conclusions

The solvent system SO_2/FSO_3H provides a useful addition to the established methods for generating radical cations, particularly at low temperatures. In the compounds we have investigated, the reaction which we interpret to be disulphuration is limited to 1,8-disubstituted naphthalenes, and is immediately apparent because of the large effect it has on the *g* value. The unusual behaviour which we observe with stilbene and diphenyl acetylene may prove to be important when it has been interpreted.

Experimental

Materials.—Hexahydropyrene (**4**), pyrene (**5**), perylene (**6**), acenaphthene (**17**), (*Z*)-stilbene, acetoin, durene (**9**) (Aldrich) and (*E*)-stilbene, and sulphur dioxide (BDH) were used as received. Diphenylacetylene (**20**) (Aldrich) was recrystallised from ethanol, and anthracene (**1**) from chloroform. Pentamethylcyclopentadiene (**8**) (Aldrich) was purified by column chromatography and dihydrophenalene (**13**) (K and K) by preparative t.l.c. Pyracene (**3**) and 5,6-dimethylacenaphthene (**7**) were prepared by the method of Capino and Gowecki,[44] and 2,2-dimethyl-4,5-benzodioxolane (**12**) from the reaction of catechol with acetone in the presence of toluene-*p*-sulphonic acid.[45] Dichloromethane (BDH) was distilled from P_2O_5 under nitrogen and fluorosulphonic acid (BDH) was distilled under nitrogen.

E.S.R. Spectroscopy.—Sulphur dioxide (*ca.* 0.4 cm^3) was condensed under nitrogen into a silica e.s.r. tube at 203 K. Fluorosulphonic acid (0.4 cm^3) was added, then a stream of dry nitrogen was passed through the solution to remove oxygen. The substrate (*ca.* 10 mg) in dichloromethane was added to the solvent, the tube was sealed, and inserted into the cavity at 203 K. Compounds (**1**)–(**4**), (**6**), and (**7**) gave strong spectra immediately; compounds (**5**) and (**11**) required warming to *ca.* 233 K, and compounds (**8**)–(**10**) and (**12**) required photolysis (> 300 nm) at 233 K.

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