# An EPR study of electron transfer reactions involving arenes and mercury(II) or thallium(III) salts

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***Received (in Cambridge) 25th August 1998, Accepted 27th October 1998***

EPR Spectroscopic evidence has been found for a number of new examples of the recently-recognised alternative mechanism of arene mercuriation in which collapse of the $ArH^{\bullet +}$ $Hg(TFA)_2^{\bullet -}$ radical ion pair leads to the formation of the arylmercury trifluoroacetate $ArHg(TFA)^{\bullet +}$. The mercury is always introduced at the position where the EPR hyperfine coupling $a$(H) in the parent $ArH^{\bullet +}$ is largest, and the ratio between the coupling constants of the mercury which has been introduced and the hydrogen which has been displaced, $a(^{119}Hg–TFA)/a(^{1}H)$ is normally about 20.6.

The magnitude of $a(^{119}Hg–TFA)$ in $ArHg(TFA)^{\bullet +}$ is interpreted in terms of the state of hybridisation of the mercury, where the amount of *s* character in the Ar–Hg bond, which is determined by the number and nature of the other ligands about the mercury, affects the transfer of electron spin by the spin polarisation mechanism.

When the mercury is flanked by oxygen in dioxolane or dioxane rings, the value of $a(^{119}Hg)/a(^{1}H)$ is low, and it is suggested that this is caused by an increase in the coordination state of the mercury.

Addition of fluorosulfonic acid to these trifluoroacetates $ArHg(TFA)^{\bullet +}$ often gives the corresponding fluorosulfonates $ArHgOSO_2F^{\bullet +}$, in which the ratio $a(^{119}HgOSO_2F)/a(^{119}HgTFA)$ is about 1.15. This increase in $a(^{119}Hg)$ is thought to result from rehybridisation of the mercury induced by the more electronegative fluorosulfonate ligand, putting more *s* character into the Ar–Hg bond.

Oxidation of a number of arenes with thallium(III) tris(trifluoroacetate) has provided one further example of the formation of aryl trifluoroacetate radical cations $Ar(TFA)^{\bullet +}$, and it is suggested that these are formed by the reductive elimination reaction of thalliated intermediates, $ArTl(TFA)_2$.

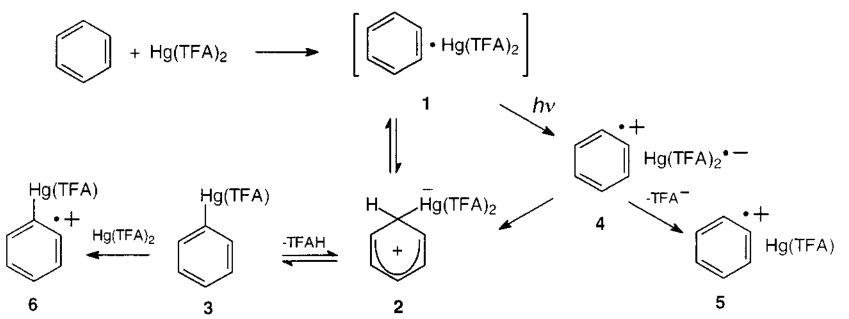
## Introduction

A variety of reactions can occur in sequence when an arene, represented by benzene in Scheme 1, is treated with mercury(II) bis(trifluoroacetate) [$Hg(TFA)_2$] in trifluoroacetic acid (TFAH). A charge transfer complex **1** is first formed, and one example has been isolated and characterised by X-ray crystallography.[1] The $Hg(TFA)_2$ may then electrophilically attack the arene to give the Wheland complex **2**, which loses TFAH to give the arylmercury(II) trifluoroacetate **3**.[2] However, if the charge transfer complex **1** is irradiated in its absorption band, electron transfer may be induced to give the radical ion pair, **4**; back electron transfer is avoided by dissociation of the counter anion $Hg(TFA)_2^{\bullet -}$, and the EPR spectrum of the radical cation **5** can be observed.[3] With some easily oxidised arenes the electron transfer **1**→**4** may occur in the dark.

The former of these processes represents the mechanism which is commonly accepted for aromatic mercuriation,[2] and the latter process has been very widely used in EPR studies of radical cations derived from arenes and other π-electron systems.[4]

In 1987 we found that with a number of the arenes under photolytic conditions, EPR spectra of the corresponding arylmercury radical cations **6** resulting from mercurideprotonation developed, whereas no mercuriation occurred in the dark.[5–7] It appears that collapse of the $ArH^{\bullet +}$ $Hg(TFA)_2^{\bullet -}$ radical ion pair **4** provides an alternative route to the Wheland complex **2** and thence to ArHg(TFA) **3** and $ArHg(TFA)^{\bullet +}$ **6**.

Arene radical cations can also be generated from the arene and thallium(III) tris(trifluoroacetate) in trifluoroacetic acid.[8] The mechanism of the reaction was suggested to be similar to that for oxidation with mercury(II) as shown in Scheme 2,[8] but Eberson has proposed that the mechanism is more complex.[9] Arylthallium(III) radical cations $7^{\bullet +}$ have never been directly observed in these reactions, but the reaction of anthracene gives rise to the spectrum of the radical cations of 9-trifluoroacetoxy- and 9,10-bis(trifluoroacetoxy)anthracene,[10–12] benzo[*a*]pyrene, 7-methylbenzo[*a*]pyrene, and 12-methylbenzo[*a*]pyrene show the spectrum of the radical cations of the 7- and/or 12-trifluoroacetates,[13] and triptycene (9,10-dihydro-9,10-[1,2]benzenoanthracene) shows a spectrum which was ascribed to the radical cation of tris(trifluoroacetoxy)triptycene,[12] and it was suggested that these trifluoroacetates might be formed *via* the thalliated intermediate **7** (Scheme 2).[12]

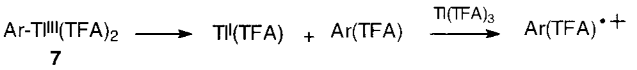


Scheme 1

**Table 1** EPR Spectra of arene and arylmercury radical cations in $Hg(TFA)_2$ at 260 K

| Radical cation | $a$/G | | $g$-factor | $a$(Hg)/$a$(H) | $a(HgO_3SF)/a[Hg(TFA)]$ |
|---|---|---|---|---|---|
| **8**$^{\cdot+}$ | 0.20 (4Hα) | 0.36 (4Hβ) | 2.0025 | | |
| **8a**$^{\cdot+}$ | 0.20 (4Hα) | 0.36 (3Hβ)<br>76.71 [Hg(TFA)] | 2.0014 | 21.3 | |
| **8b**$^{\cdot+}$ | 0.20 (4Hα) | 0.36 (3Hβ)<br>88.15 ($HgO_3SF$) | 2.0014 | 24.5 | 1.150 |
| **9**$^{\cdot+}$ | 5.50 (3H, Me)<br>2.97 (1Hβ)<br>3.56 (1Hβ)<br>4.20 (1Hβ) | 0.18 (1Hα)<br>0.55 (1Hα)<br><0.05 (2Hα) | 2.0026 | | |
| **9a**$^{\cdot+}$ | 5.20 (3H, Me)<br>3.00 (1Hβ)<br>3.60 (1Hβ) | 0.18 (1Hα)<br>0.55 (1Hα)<br>91.85 [Hg(TFA)] | 2.0018 | 21.8 | |
| **9b**$^{\cdot+}$ | 5.20 (3H, Me)<br>3.00 (1Hβ)<br>3.60 (1Hβ) | 0.18 (1Hα)<br>0.55 (1Hα)<br>104.83 ($HgO_3SF$) | 2.0018 | 24.9 | 1.142 |
| **10**$^{\cdot+}$ | <0.15 (12Hα) | 3.25 (4Hβ) | 2.0025 | | |
| **10a**$^{\cdot+}$ | <0.15 (12Hα) | 3.25 (3Hβ)<br>69.86 [Hg(TFA)] | 2.0014 | 21.5 | |
| **10b**$^{\cdot+}$ | <0.15 (12Hα) | 3.25 (3Hβ)<br>80.28 ($HgO_3SF$) | 2.0014 | 24.7 | 1.149 |
| **11**$^{\cdot+}$ | <0.005 (4Hα) | 2.20 (4Hβ) | 2.0039 | | |
| **11a**$^{\cdot+}$ | <0.005 (4Hα) | 2.20 (3Hβ)<br>43.20 [Hg(TFA)] | 2.0031 | 19.6 | |
| **11b**$^{\cdot+}$ | <0.005 (4Hα) | 2.20 (3Hβ)<br>49.30 ($HgO_3SF$) | 2.0031 | 22.4 | 1.143 |
| **12**$^{\cdot+}$ | 2.48 (4H)<br>11.60 (2H) | 0.95 (2H, Ar) | 2.0046 | | |
| **12a**$^{\cdot+}$ | 2.48 (4H)<br>11.70 (2H) | 13.72 [2Hg(TFA)] | 2.0052 | 14.6 | |
| **12b**$^{\cdot+}$ | 2.48 (4H)<br>11.70 (2H) | 15.85 ($2HgO_3SF$) | 2.0054 | 16.9 | 1.157 |
| **13**$^{\cdot+}$ | 2.25 (8H) | 0.90 (2H, Ar) | 2.0044 | | |
| **13a**$^{\cdot+}$ | 2.25 (8H) | 12.45 [2Hg(TFA)] | 2.0048 | 13.81 | |
| **14**$^{\cdot+}$ | 7.30 (6H, Me)<br>18.04 (2H) | 0.71 (2H, Ar) | 2.0044 | | |
| **14a**$^{\cdot+}$ | 7.18 (3H, Me)<br>7.53 (3H, Me)<br>18.00 (2H) | 0.71 (1H, Ar)<br>[a] | — | | |
| **14b**$^{\cdot+}$ | 7.50 (6H, Me)<br>17.90 (2H) | 9.18 [2Hg(TFA)] | 2.0047 | 12.91 | |
| **15**$^{\cdot+}$ | 3.31 (2H-*p*)[b] | [b] | [c] | | |
| **15a**$^{\cdot+}$ | 3.31 (1H-*p*)[b] | 64.30 [Hg(TFA)] | [c] | | |
| **15b**$^{\cdot+}$ | 3.31 (1H-*p*)[b] | 74.67 ($HgO_3SF$) | [c] | | 1.161 |

[a] The $^{199}Hg$ satellites were obscured by lines due to proton coupling. [b] A detailed analysis of the proton hyperfine coupling was not possible. [c] An accurate $g$-value could not be measured.



$$\underset{\mathbf{7}}{Ar\text{-}Tl^{III}(TFA)_2} \longrightarrow Tl^{I}(TFA) + Ar(TFA) \xrightarrow{Tl(TFA)_3} Ar(TFA)^{\bullet+}$$

Scheme 2

To date, mercuriated arene radical cations have been reported from biphenylene,[6] acenaphthene, pyracene, hexahydropyrene, triptycene, *p*-terphenyl, tetramethylnaphthopyran, anthracene, dibenzodioxin[12] and 4-*tert*-butylanisole.[14] Sometimes progressive multiple mercuriation is observed; for example, the mono-, di-, tri-, and tetra-mercuriated radical cations have been characterised from diphenylene[6] and dibenzodioxin.[15] Mercuriation always occurs at the site where the local coefficient of the Hückel HOMO of the hydrocarbon is greatest (as it also does when mercuriation occurs under thermal, kinetically controlled, conditions), and there is a constant ratio of about 20.6 between the hyperfine coupling by the $^{199}Hg$ ($I$ 1/2, abundance 16.84%) which has been introduced, and by the proton which has been displaced.[15] In all these examples, mercuriation brings about a reduction in the $g$-value of the radical cation. The radical cation of 4-*tert*-butylanisole, however, cannot be examined against these rules as the spectrum of the pre-mercuriated radical cation, or the $g$-value of the mercuriated product, have not been reported.

We now report the extension of these studies to further aromatic systems, and have investigated the effect on the EPR spectra of varying the group X in the radical cations $ArHgX^{\cdot+}$. A number of oxygenated arenes have also been oxidised using the $Tl(TFA)_3$–TFAH reagent in a search for examples of thalliated arene radical cations or further examples of trifluoroacetoxylated radical cations.

## Results

### Oxidations with $Hg(TFA)_2$–TFAH

**Biphenylene 8.** A solution of biphenylene **8** in trifluoroacetic acid containing mercury(II) trifluoroacetate at 260 K had a light orange colour and showed, without photolysis, the familiar spectrum of the radical cation (Fig. 1);[6] details of the spectra are given in Table 1. When this solution was irradiated with UV light filtered through Pyrex glass and through metal gauze which reduced the intensity to 10%, the spectrum of the radical cation of the arylmercury trifluoroacetate **8a**$^{\cdot+}$ developed with $a(^{199}Hg)$ 76.61 G. When monomercuriation was complete, the sample tube was removed from the cavity, and a few drops of fluorosulfonic acid ($FSO_3H$) were added, as the sample was maintained at 260 K under a stream of nitrogen. A white precipitate of $Hg(O_3SF)_2$ separated. The sample was returned to the cavity, when, without photolysis it showed the spectrum of

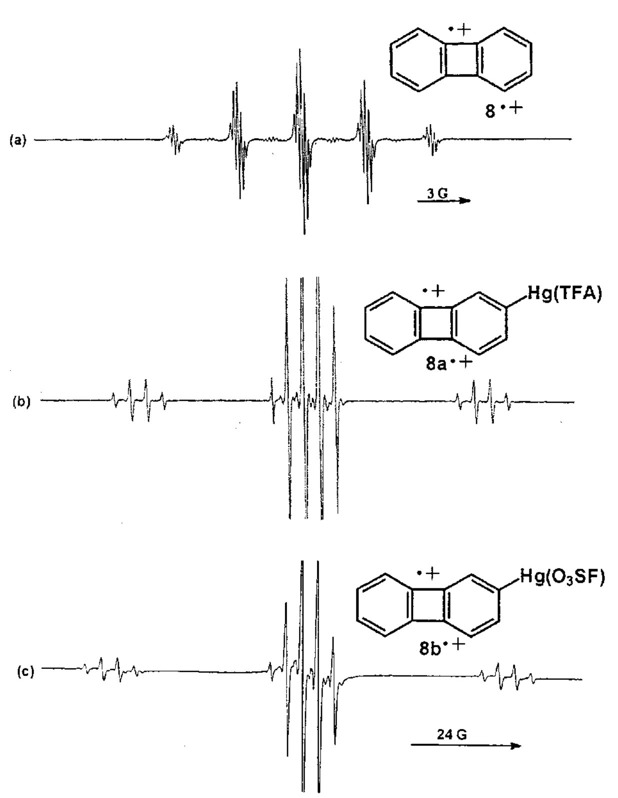
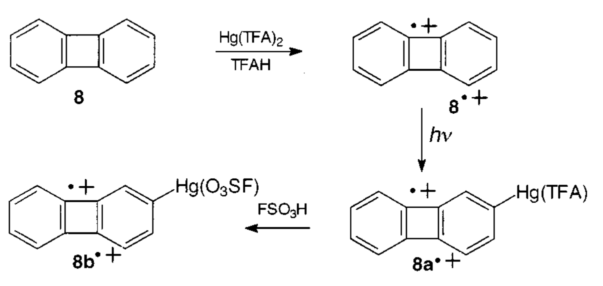


**Fig. 1** EPR Spectra of radical cations in TFAH at 260 K: (a) biphenylene $8^{\bullet+}$, (b) its mercury trifluoroacetate $8a^{\bullet+}$, and (c) its mercury fluorosulfonate $8b^{\bullet+}$.



$8^{\bullet+}$. Upon irradiation a new spectrum developed with *a*($^{199}$ Hg) 88.15 G, *g* 2.0014, which we ascribe to the radical cation of the arylmercury fluorosulfonate $8b^{\bullet+}$ (Fig. 1). Prolonged photolysis restored the spectrum of $8^{\bullet+}$, presumably as a result of protodemercuriation of $8b^{\bullet+}$.

Similar experiments with acids other than $FSO_3H$ did not generate any new spectra: methanesulfonic acid and trifluoromethanesulfonic acid gave rise to a spectrum with the characteristics of $8a^{\bullet+}$, and hydrogen chloride, chlorosulfonic acid, and sulfuric acid gave only the parent radical cation $8^{\bullet+}$. It is rather surprising that $CF_3SO_3H$ apparently did not convert the arylmercury trifluoroacetate into the arylmercury trifluoromethanesulfonate since Deacon has shown that $Hg(TFA)_2$ in TFAH reacts with $CF_3SO_3H$ to give $Hg(O_3SCF_3)_2$, and that this system reacts even with deactivated arenes to give the arylmercury trifluoromethanesulfonates.[16]

**2-Methylbiphenylene 9.** Photolysis of a solution of 2-methylbiphenylene in dichloromethane containing $AlCl_3$ at 243 K gave rise to a strong spectrum of the radical cation $9^{\bullet+}$ (Fig. 2 and Table 1). A solution of **9** in $Hg(TFA)_2$–TFAH at 260 K showed the same spectrum of $9^{\bullet+}$ without photolysis. When this sample was photolysed with filtered UV light, $^{199}$Hg satellites developed with *a*($^{199}$Hg) 91.85 G, and after *ca.* 10 min the spectrum showed that monomercuriation to give $9a^{\bullet+}$ was complete. Continued photolysis caused further mercuriation, but unfortunately the spectrum was not strong enough for the satellites due to dimercuriation to be identified. Monomercurideprotonation occurs at the β-position which shows *a*(1H) 4.20 G, but which of the three available β-positions this represents is uncertain.

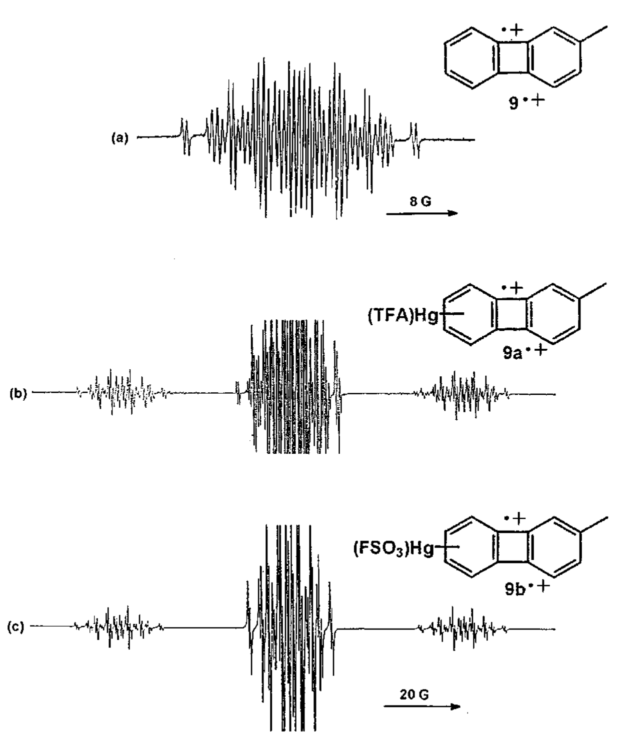
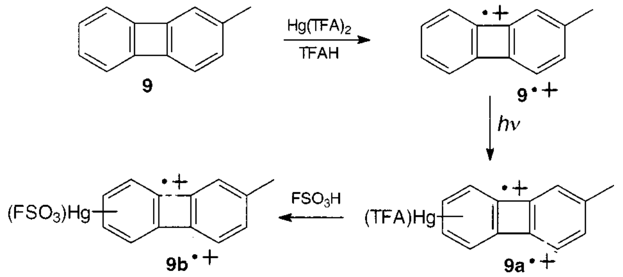


**Fig. 2** EPR Spectra of radical cations in TFAH at 260 K: (a) 2-methylbiphenylene $9^{\bullet+}$, (b) its mercury trifluoroacetate $9a^{\bullet+}$, and (c) its mercury fluorosulfonate $9b^{\bullet+}$.

A few drops of $FSO_3H$ were added to the solution of $9a^{\bullet+}$; photolysis with filtered UV light then gave rise to a weak spectrum of the arylmercury fluorosulfonate $9b^{\bullet+}$, with *a*($^{199}$Hg) 104 G, but after about 2 min this was replaced by the spectrum of the parent hydrocarbon $9^{\bullet+}$.



**1,4,5,8-Tetramethylbiphenylene 10.** The quintet spectrum of the radical cation $10^{\bullet+}$, formed by oxidation with $Tl(TFA)_3$ in TFAH, has already been reported (Table 1);[17] any hyperfine coupling by the methyl groups is lost in the line width. The same spectrum (Fig. 3) is obtained by oxidation with $Hg(TFA)_2$ in TFAH. Irradiation of this solution with filtered UV light showed that mercurideprotonation occurred to give $10a^{\bullet+}$, with reduction of the quintet to a quartet and the development of mercury satellites with *a*($^{199}$Hg) 69.86 G. When monomercuriation was complete, a few drops of $FSO_3H$ were added. Photolysis now showed a central spectrum consisting of the original quintet and an overlapping quartet with quartet satellites with *a*($^{199}$Hg) 80.28 G. Again we ascribe this spectrum to the arylmercury fluorosulfonate, $10b^{\bullet+}$. On prolonged photolysis the quartet spectrum and its satellites were lost, presumably because of protodemercuriation.

**Dibenzodioxin 11.** Dibenzodioxin in TFAH containing $Tl(TFA)_3$ gave a blue solution which showed at 260 K a strong

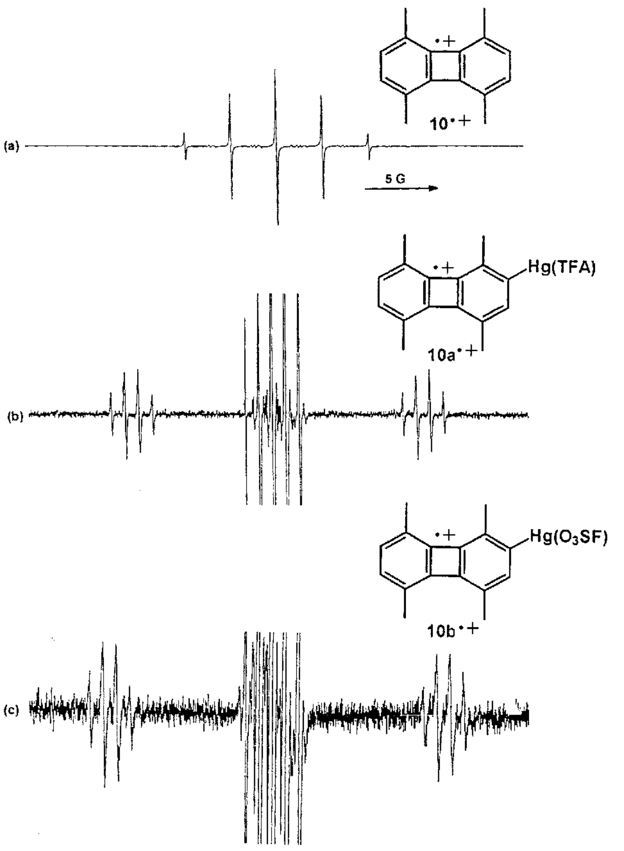
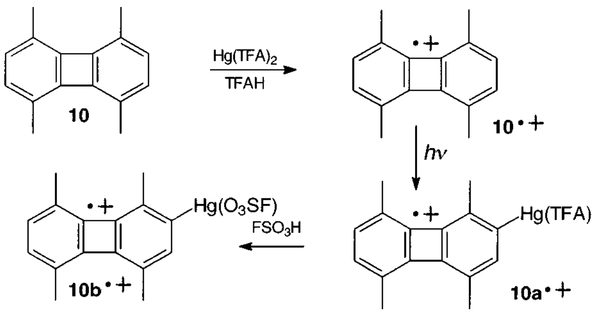
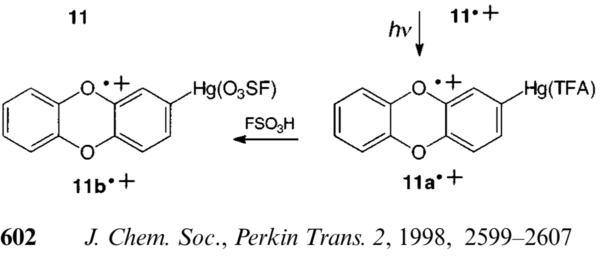


**Fig. 3** EPR Spectra of radical cations in TFAH at 260 K: (a) 1,4,5,8-tetramethylbiphenylene **10**$^{•+}$, (b) its mercury trifluoroacetate **10a**$^{•+}$, and (c) its mercury fluorosulfonate **10b**$^{•+}$.



quintet spectrum of the radical cation **11**$^{•+}$ (Fig. 4 and Table 1). A solution in TFAH containing Hg(TFA)$_2$ was yellow, and, without photolysis, showed the same quintet spectrum of **11**$^{•+}$. Photolysis of this with filtered UV light caused mercuride-protonation and the development of the spectrum of **11a**$^{•+}$ as a quartet with mercury satellites, $a$($^{199}$Hg) 43.20 G.[12] After 15 min the spectrum showed that monomercuriation was complete. A few drops of FSO$_3$H were then added, and photolysis gave rise to the spectrum of the fluorosulfonate **11b**$^{•+}$, with $a$($^{119}$Hg) 49.30 G.



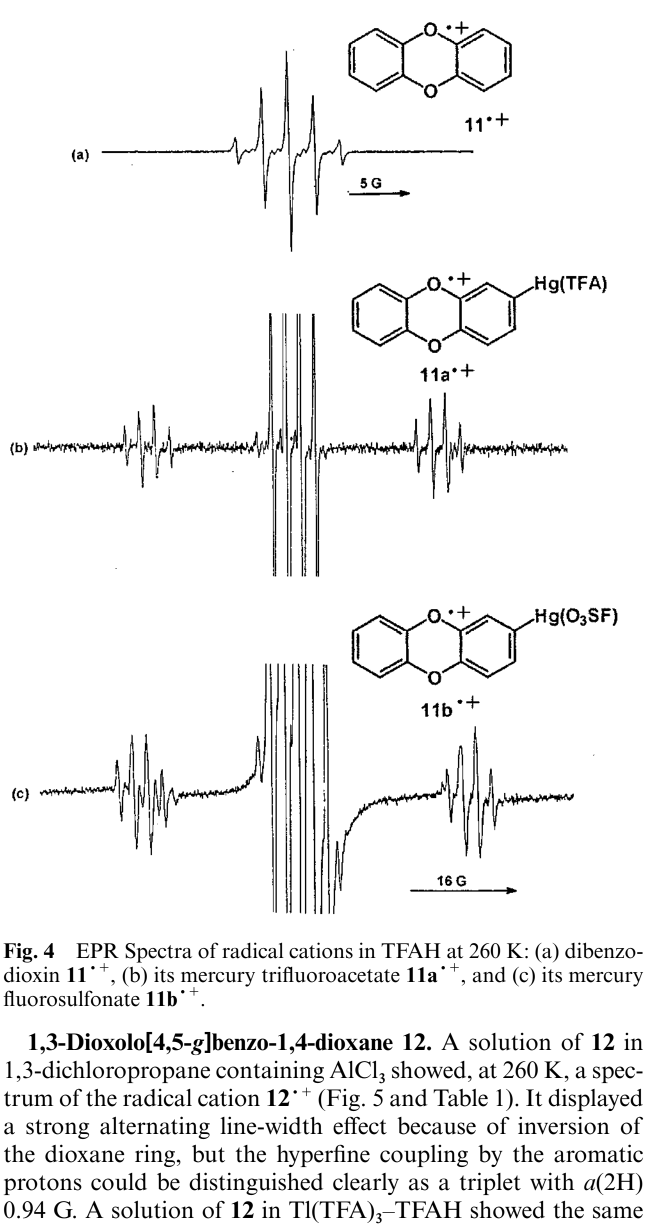
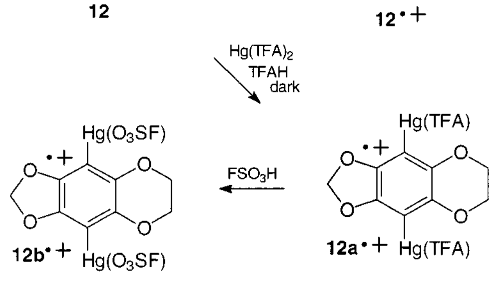


**Fig. 4** EPR Spectra of radical cations in TFAH at 260 K: (a) dibenzodioxin **11**$^{•+}$, (b) its mercury trifluoroacetate **11a**$^{•+}$, and (c) its mercury fluorosulfonate **11b**$^{•+}$.

**1,3-Dioxolo[4,5-*g*]benzo-1,4-dioxane 12.** A solution of **12** in 1,3-dichloropropane containing AlCl$_3$ showed, at 260 K, a spectrum of the radical cation **12**$^{•+}$ (Fig. 5 and Table 1). It displayed a strong alternating line-width effect because of inversion of the dioxane ring, but the hyperfine coupling by the aromatic protons could be distinguished clearly as a triplet with $a$(2H) 0.94 G. A solution of **12** in Tl(TFA)$_3$–TFAH showed the same spectrum. However, if **12** was dissolved in TFAH containing Hg(TFA)$_2$, it showed immediately, without photolysis, the spectrum of the dimercuriated radical cation **12a**$^{•+}$ with $a$($^{119}$Hg) 13.72 G (Fig. 5). At 333 K, all four of the protons in the dioxine ring became equivalent, and a satisfactory simulation could be obtained (Fig. 5).

A few drops of fluorosulfonic acid were added to the solution of **12a**$^{•+}$, then photolysis with filtered UV light gave rise to a spectrum with $a$($^{119}$Hg) 15.85 G which we ascribe to the arylmercury fluorosulfonate **12b**$^{•+}$.



**Benzo[1,2-*b*:4,5-*b*′]bis-1,4-dioxane 13.** Benzo[1,2-*b*:4,5-*b*′]-bis-1,4-dioxane in 1,3-dichloropropane containing AlCl$_3$ at

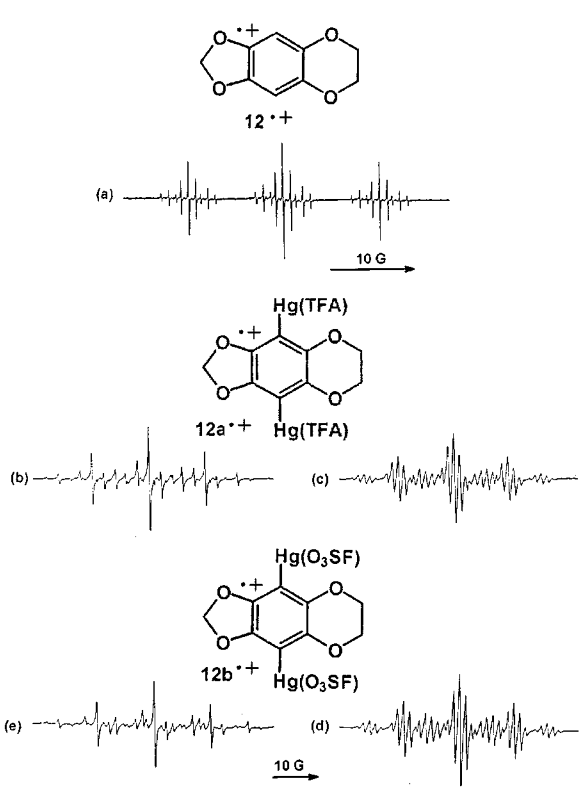
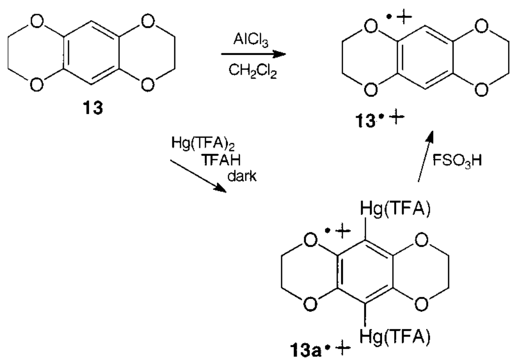


**Fig. 5** EPR Spectra of radical cations in TFAH: (a) 1,3-dioxolo[4,5-*g*]-benzo-1,4-dioxane **12**$^{•+}$ at 260 K, (b) its bis(mercury trifluoroacetate) **12a**$^{•+}$ at 260 K, (c) **12**$^{•+}$ at 333 K, (d) computer simulation of spectrum (c), (e) the bis(mercury fluorosulfonate) **12b**$^{•+}$ at 260 K.

260 K gave a yellow solution which showed a series of temperature-dependent spectra resulting from conformational inversion of the dioxine rings in **13**$^{•+}$. A solution of **13** in TFAH–Hg(TFA)$_2$ at 260 K was yellow, and in the dark it showed a weak EPR spectrum of the dimercuriated radical cation **13a**$^{•+}$ with *a*($^{199}$Hg 12.72 G), and this spectrum became stronger when the sample was irradiated with filtered UV light. At 330 K, the axial and equatorial protons of the methylene groups became equivalent, and a satisfactory simulation of the spectrum could be obtained (Fig. 6). When a few drops of fluorosulfonic acid were added, the spectrum of the protodemercuriated parent **13**$^{•+}$ was restored, and no mercuriated species could be detected, even on photolysis.



**5,6-Dimethylbenzo-1,3-dioxole 14.** A solution of 5,6-dimethylbenzo-1,3-dioxole in Tl(TFA)$_3$–TFAH showed a strong EPR spectrum of the radical cation **14**$^{•+}$ without photolysis. In Hg(TFA)$_2$–TFAH, **14** gave a yellow solution which showed no EPR spectrum in the dark. On photolysis the spectrum of the monomercuriated radical cation **14a**$^{•+}$ developed (Table 1 and Fig. 7) but the main $^{199}$Hg satellites lie within the body of the complicated spectrum, and the value of *a*($^{199}$Hg) could not be extracted. On prolonged photolysis, this spectrum was replaced by that of the dimercuriated radical cation **14b**$^{•+}$ (Fig. 7) with *a*($^{199}$Hg) 9.18 G. When fluorosulfonic acid was added to this solution, a white precipitate of Hg(O$_3$SF)$_2$ separated, and only the spectrum of the parent **14**$^{•+}$ could be observed.

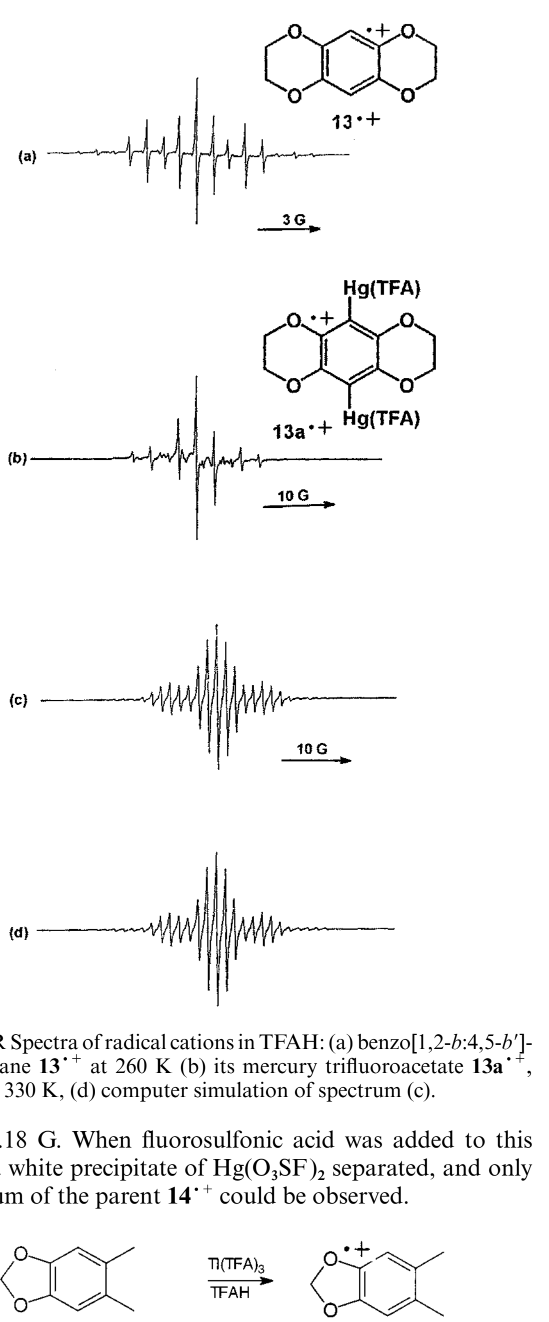
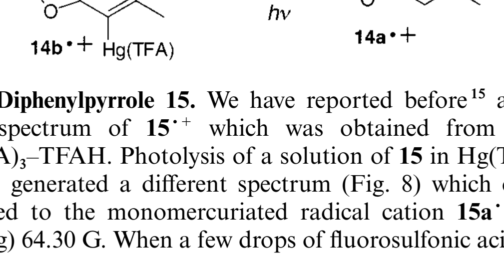


**Fig. 6** EPR Spectra of radical cations in TFAH: (a) benzo[1,2-*b*:4,5-*b*′]-bis-1,4-dioxane **13**$^{•+}$ at 260 K (b) its mercury trifluoroacetate **13a**$^{•+}$, (c) **13a**$^{•+}$ at 330 K, (d) computer simulation of spectrum (c).



**2,5-Diphenylpyrrole 15.** We have reported before[15] a weak EPR spectrum of **15**$^{•+}$ which was obtained from **15** in Tl(TFA)$_3$–TFAH. Photolysis of a solution of **15** in Hg(TFA)$_2$–TFAH generated a different spectrum (Fig. 8) which can be assigned to the monomercuriated radical cation **15a**$^{•+}$ with *a*($^{199}$Hg) 64.30 G. When a few drops of fluorosulfonic acid were added, photolysis gave rise to a spectrum with *a*($^{199}$Hg) 74.67 G (Fig. 8).

### Oxidations with Tl(TFA)$_3$–TFAH

In a search for the first examples of the spectra of arylthallium radical cations, and for further examples of trifluoroacetoxyl-

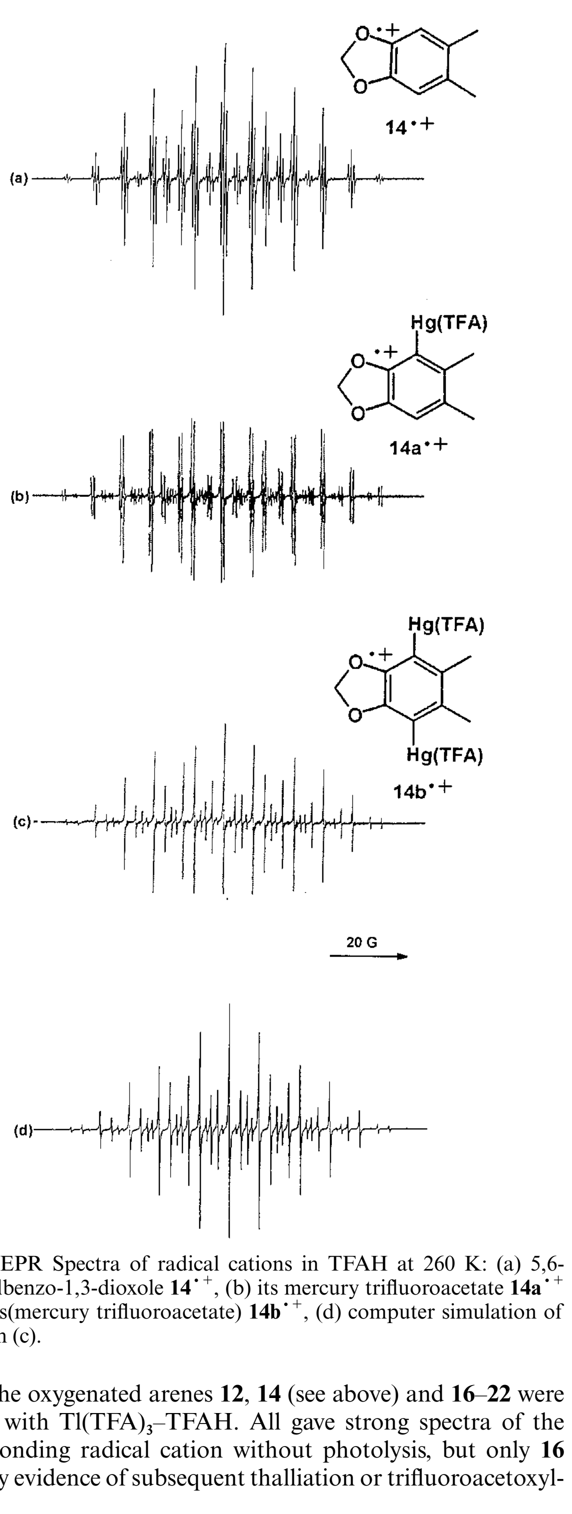


**Fig. 7** EPR Spectra of radical cations in TFAH at 260 K: (a) 5,6-dimethylbenzo-1,3-dioxole **14**$^{\bullet+}$, (b) its mercury trifluoroacetate **14a**$^{\bullet+}$ (c) its bis(mercury trifluoroacetate) **14b**$^{\bullet+}$, (d) computer simulation of spectrum (c).

ation, the oxygenated arenes **12**, **14** (see above) and **16**–**22** were treated with Tl(TFA)$_3$–TFAH. All gave strong spectra of the corresponding radical cation without photolysis, but only **16** gave any evidence of subsequent thalliation or trifluoroacetoxylation.

**4,7-Di-*tert*-butylbenzo-1,3-dioxole 16.** In the dark, a solution of 4,7-di-*tert*-butylbenzo-1,3-dioxole in dichloromethane containing AlCl$_3$ showed a strong spectrum of the radical cation **16**$^{\bullet+}$ with *g* 2.0047 (Table 1 and Fig. 9). In Hg(TFA)$_2$–TFAH **16** gave a yellow solution which showed a strong spectrum of **16**$^{\bullet+}$; when this solution was irradiated with filtered UV light, the intensity of the spectrum diminished, but under no conditions of temperature or photolysis could we observe the distortion of the spectrum or the appearance of satellites which would indicate the onset of mercuriation.

In Tl(TFA)$_3$–TFAH, **16** gave a yellow solution which, without photolysis, gave initially the spectrum of **16**$^{\bullet+}$. After about 5 min a second spectrum developed in the gaps of the first, and after 30 min the spectrum shown in Fig. 9 was obtained, with hyperfine coupling to only one aromatic proton, and an increased *g*-factor of 2.0048. After a total of 1.5 h, the spectrum was lost. The absence of any discernible $^{203/205}$Tl hyperfine coupling ($^{203}$Tl, 29.52% abundance, *I* 1/2, $^{205}$Tl, 70.48% abundance, *I* 1/2) appears to rule out the possibility that the missing aromatic proton has been replaced by thallium, and we assign this spectrum to the trifluoroacetate **16a**$^{\bullet+}$. The rate of this trifluoroacetoxylation reaction was markedly increased when trifluoroacetic anhydride was added to the solution, perhaps because it removed traces of adventitious moisture.

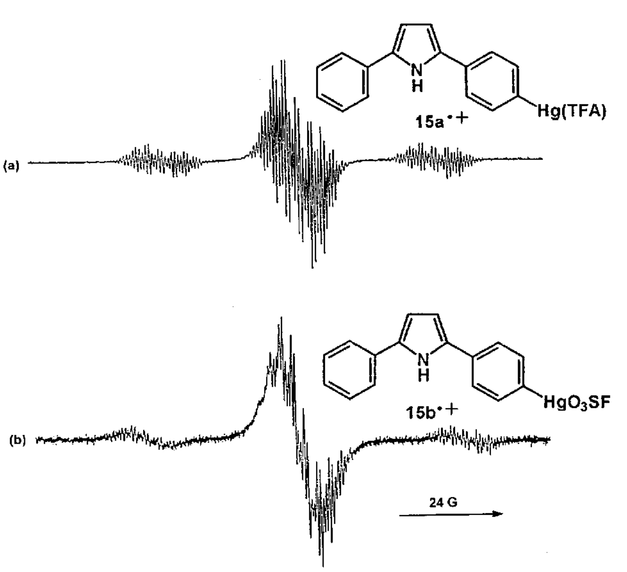
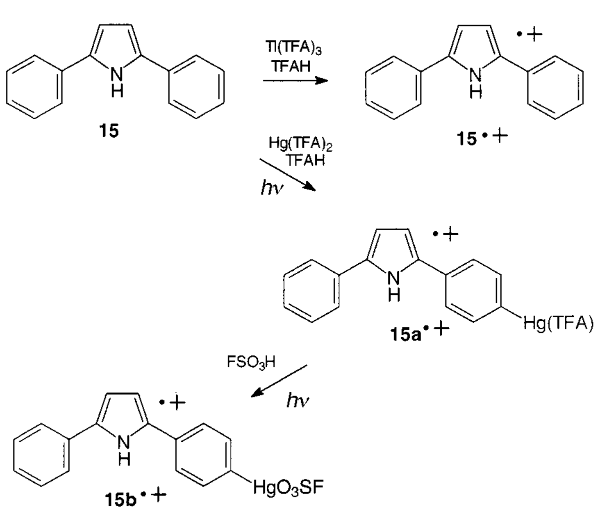
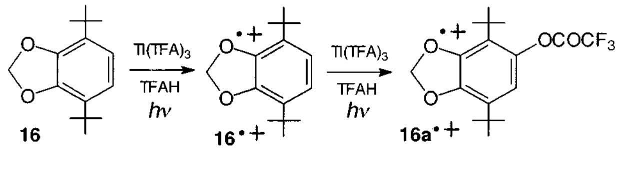


**Fig. 8** EPR Spectra of radical cations in TFAH at 260 K: (a) the mercury trifluoroacetate from 2,5-diphenylpyrrole, **15a**$^{\bullet+}$, (b) the mercury fluorosulfonate, **15b**$^{\bullet+}$.



Details of the spectra of the radical cations derived from **16**–**22** are given in Table 2. The spectra of some of these radical cations have been reported previously; the spectra of **17**$^{\bullet+}$ and **18**$^{\bullet+}$ were observed by Fleischhauer using a cerium(IV) flow system,[18] and that of **21**$^{\bullet+}$ by Sullivan using AlCl$_3$–MeNO$_2$.[19] Bubnov observed the spectrum of **22**$^{\bullet+}$ using the Tl(TFA)$_3$–TFAH reagent.[20] Our data agree with those previously reported. We also obtained the same spectrum of **22**$^{\bullet+}$, with no indication of mercuriation, by photolysis of **22** in Hg(TFA)$_2$–TFAH at 260 K.



The tribenzodehydroannulene **23** was interesting, not only

**Table 2** EPR Spectra of arene radical cations in Tl(TFA)$_3$–TFAH at 260 K

| Radical cation | *a*/G | | *g*-factor |
|---|---|---|---|
| $\mathbf{16}^{\bullet +}$ | 21.41 (2H) | 4.55 (2H, Ar) | 2.0047 |
| $\mathbf{16a}^{\bullet +}$ | 21.71 (2H) | 4.00 (1H) | 2.0048 |
| $\mathbf{17}^{\bullet +}$ | 9.02 (4H) | 3.05 (2H) | 2.0037 |
| $\mathbf{18}^{\bullet +}$ | 11.79 (4H) | 1.03 (2H, Ar) | 2.0042 |
| $\mathbf{19}^{\bullet +}$ | 11.41 (2H)<br>2.22 (6H) | 0.96 (2H, Ar) | 2.0042[a] |
| $\mathbf{20}^{\bullet +}$ | 3.01 (6H, OMe)<br>7.22 (6H, Me) | 0.58 (2H, Ar) | 2.0034 |
| $\mathbf{21}^{\bullet +}$ | 2.20 (12H, OMe) | 0.86 (2H, Ar) | 2.0040 |
| $\mathbf{22}^{\bullet +}$ | 2.09 (6H, OMe) | 4.17 (2H, Ar) | 2.0041[b] |
| $\mathbf{23}^{\bullet +}$ | 1.29 (6H) | | 2.0025 |

[a] The same persistent spectra were obtained using AlCl$_3$–CH$_2$Cl$_2$ and FSO$_3$H–SO$_2$. [b] The same spectrum was obtained using Hg(TFA)$_2$–TFAH.

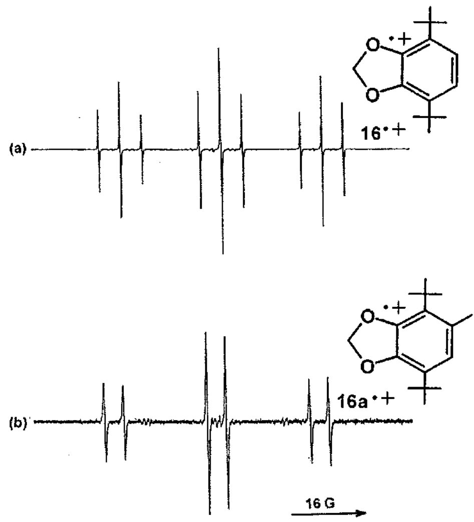


**Fig. 9** EPR Spectra of radical cations in TFAH at 260 K: (a) 4,7-di-*tert*-butylbenzo-1,3-dioxole $\mathbf{16}^{\bullet +}$, (b) its trifluoroacetate, $\mathbf{16a}^{\bullet +}$.

because the radical cation might show evidence of aromatic metallation, but also because of the special properties of arylalkyne radical cations. Dialkylalkyne radical cations react with their parents to give tetraalkylcyclobutadiene radical cations[21,22] but diarylalkynes on oxidation show the spectra of triarylazulene radical cations;[23] the radical anions of diarylalkynes on the other hand do not rearrange. It seemed possible that **23** might show this ring-expansion behaviour, or perhaps that intramolecular trimerisation might give the tris(cyclobutadiene) **24**.

Reduction of **23** with potassium and a small amount of benzo-18-crown-6 in THF at 243 K gave a light blue solution which showed a spectrum consisting of a septet of septets, *a*(6H) 1.38, *a*(6H) 0.10 G, *g* 2.0026. Brunner *et al.*[24] have reported a similar but weaker spectrum with *a*(6H) 1.34, *a*(6H) 0.09 G by reduction of **23** with potassium in dimethoxyethane at 298 K. Oxidation of **23** with Tl(TFA)$_3$–TFAH gave the simple septet spectrum (Table 2) which is shown in Fig. 10.

## Discussion

### EPR Spectra of the substrate radical cations

The small hyperfine coupling to the aromatic protons in the radical cations $\mathbf{12}^{\bullet +}$, $\mathbf{13}^{\bullet +}$, $\mathbf{14}^{\bullet +}$, $\mathbf{18}^{\bullet +}$, $\mathbf{19}^{\bullet +}$, $\mathbf{20}^{\bullet +}$, and $\mathbf{21}^{\bullet +}$, and the relatively large coupling to the aromatic protons in $\mathbf{16}^{\bullet +}$ and $\mathbf{22}^{\bullet +}$, show that the *ortho* oxygen substituents from the dioxine rings break the degeneracy of the orbitals of the benzene ring to confer $\psi_A$ character on the SOMO. The large coupling to the methylene protons of the dioxole rings in $\mathbf{12}^{\bullet +}$, $\mathbf{14}^{\bullet +}$, $\mathbf{16}^{\bullet +}$, $\mathbf{18}^{\bullet +}$, and $\mathbf{19}^{\bullet +}$, provides further examples of the Whiffen effect which results from the flanking oxygen atoms having the same sign of the SOMO coefficient.[25] The spectra of the radical cations of all these dioxoles were clean and strong and showed no signs of the dimerization or ring-opening which Eberson has observed with other 1,3-benzodioxoles.[14] The temperature-dependent spectra which are obtained from compounds **12** and **13** make it possible to determine the energy barrier to inversion of the dioxine rings, and a kinetic EPR study of these, and a number of other compounds, is the subject of a separate report.[26]

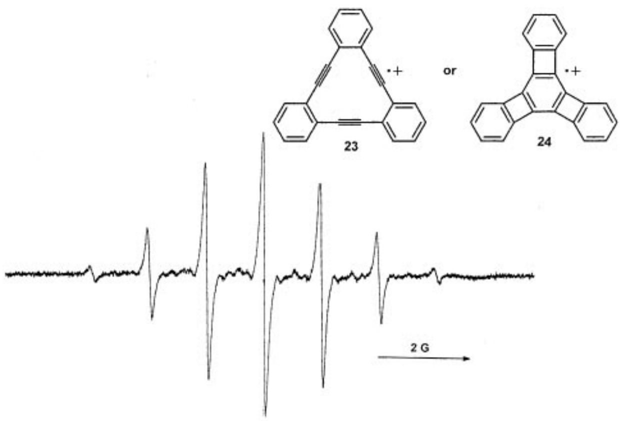
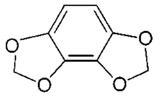
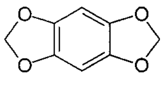


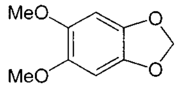
**Fig. 10** EPR Spectrum of the radical cation obtained from a solution of tribenzocyclodecatrienetriyne **23** in Hg(TFA)$_2$–TFAH at 260 K.



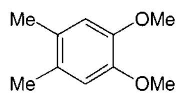
**17**



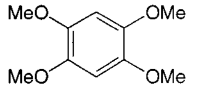
**18**



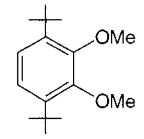
**19**



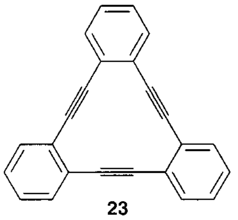
**20**



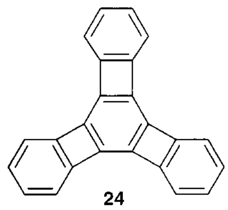
**21**



**22**



**23**



**24**

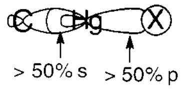
The simple septet spectrum (Table 2 and Fig. 10) which is observed when **23** is oxidised with Tl(TFA)$_3$–TFAH excludes the possibility that mercuriation has occurred (which would result in a basic sextet) or that an azulene has been formed (which would give a much more complicated spectrum). The surprising feature is that the coupling constants in the radical cation are *less* than those in the radical anion, whereas the reverse situation usually holds in an alternant hydrocarbon.[27] This leaves open the possibility that cyclisation has taken place to give $\mathbf{24}^{\bullet +}$; **24** is a known compound,[28] and it would be interesting to investigate the EPR spectra of its radical anion and cation.

### Mercuriation

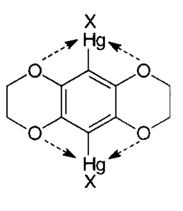
As we have observed before, mercurideprotonation always occurs to displace the proton with the highest coupling constant, that is where the local coefficient of the HOMO of the aromatic ring is greatest.[15] This is as would be expected in the radical ion pair for which **4** is the model. The mercury which is introduced has little or no effect on the hyperfine coupling constants of the remaining protons, *i.e.* on the electronic configuration of the SOMO, and multiple mercuriation may be observed when the initial substrate contains a number of equivalent positions as is the case with all of the compounds studied here. Aromatic mercuriation is reversible,[2] and the addition of a strong acid such as $FSO_3H$ to the solution which showed the EPR spectrum of ArHg(TFA)$^{\bullet+}$ sometimes regenerated the spectrum of ArH$^{\bullet+}$ presumably because protodemercuriation either of ArHg(TFA)$^{\bullet+}$ or ArHg(TFA) had occurred.

We found previously for some 20 different arylmercury radical cations that there was a constant ratio of *a*($^{199}$Hg)/*a*(H) of *ca.* 20.6 between corresponding radical cations ArHg(TFA)$^{\bullet+}$ and ArH$^{\bullet+}$, and that the mercuriation brought about a reduction of the *g*-factor by 0.0008–0.0011. The new radical cation **9a**$^{\bullet+}$, which has not been observed before, shows a value of *a*($^{199}$Hg)/*a*(H) of 21.8 and a low *g*-value, in line with these results. However the radical cations **12a**$^{\bullet+}$, **13a**$^{\bullet+}$, and **14b**$^{\bullet+}$ give ratios of *a*($^{199}$Hg)/*a*(H) of 14.6, 13.8, and 12.91, much lower than any observed before, though the values of *a*(H) are the same as those in the parent radical cations **12**$^{\bullet+}$, **13**$^{\bullet+}$, and **14**$^{\bullet+}$. Moreover, the mercuriated radical cations **12a**$^{\bullet+}$, **13a**$^{\bullet+}$, and **14b**$^{\bullet+}$ are formed with an *increase* in the *g*-values by 0.0003–0.0006.

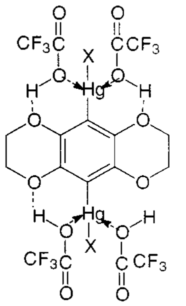
If the mercury used pure sp hybrid orbitals in bonding, the ratio *a*($^{199}$Hg)/*a*(H) would be expected to be *ca.* 15 rather than 21.[12] We have argued,[12] following Symons,[29] that this discrepancy can be understood if it is accepted that when X is electronegative, the Hg–X bond involves mainly the mercury 6p orbital, so that the C–Hg bond has an enhanced s character, and hyperfine coupling by mercury through the spin polarisation mechanism by the unpaired spin on carbon is increased as shown in **25**.



**25**



**26**



**27**

On this model, any factors which reduce the s character of the C–Hg bond would be expected to reduce the value of *a*($^{199}$Hg). The common factor between the structures of **12a**$^{\bullet+}$, **13a**$^{\bullet+}$, and **14b**$^{\bullet+}$, which do show low values of *a*($^{199}$Hg) is the presence of oxygen in the *ortho* position with respect to mercury, and one can envisage a direct or indirect ligation of the mercury as shown in **27** and **28**; both a distorted T and a pseudo tetrahedral geometry about three- or four-coordinate mercury is known,[30,31] and in either case the s character in the C–Hg bond would be reduced, and *a*($^{199}$Hg) would be smaller. No similar effect on *a*($^{199}$Hg) or the *g*-value is apparent however with the Hg(TFA) [or Hg($O_3SF$)] derivatives of dibenzodioxin **11**, which also has oxygen *ortho* to the site of mercuriation. Whatever the origin of the effect, it operates similarly in the fluorosulfonates **12b**$^{\bullet+}$ and **15b**$^{\bullet+}$ to give the linear plot shown in Fig. 11 (see below).

A plot of *a*($^{199}$Hg–$O_3SF$) against *a*($^{199}$Hg–TFA) for the fluorosulfonates **8b**$^{\bullet+}$, **9b**$^{\bullet+}$, **10b**$^{\bullet+}$, **11b**$^{\bullet+}$, **12b**$^{\bullet+}$, and **15b**$^{\bullet+}$ which show unusually high values of *a*($^{199}$Hg) is shown in Fig. 11 and has a slope of *ca.* 1.14. We use a plot against *a*($^{199}$Hg–TFA) rather than *a*(H) to avoid the apparent perturbing effect of the dioxolane or dioxane rings which is discussed above; if these anomalous compounds are neglected, the average value of *a*($^{199}$Hg)/*a*(H) is about 23.5.

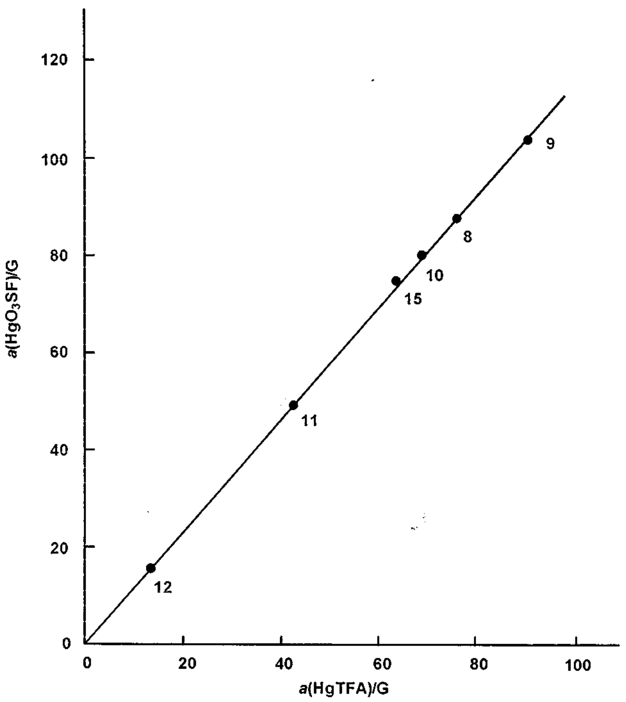


Fig. 11 Plot of *a*($^{199}$HgTFA) against *a*($^{199}$HgO$_3$SF).

Again these higher values of *a*($^{199}$Hg–$O_3SF$) can be understood on the basis of the model shown in **25**. The $FSO_3$ group is more electronegative than the $CF_3CO_2$ group, leading to an increase in p character in the Hg–$O_3SF$ bond and a balancing increase of s character in the C–Hg bond, resulting in a larger value of *a*($^{199}$Hg).

## Trifluoroacetoxylation

As before, we have observed no spectra which could be ascribed to radical cations of arylthallium compounds, ArTl(TFA)$_2$, and indeed no EPR spectra of arylthallium compounds appear to be reported in the literature. $TlX_2$ substituents are strongly electron withdrawing, so that the ionisation energy of ArTl(TFA)$_2$ is higher than that of ArH, and ArTl(TFA)$_2^{\bullet+}$ would not be observed in presence of ArH. Also, thalliodeprotonation, like mercurideprotonation, is reversible,[2] and the arylthallium compounds may not persist under our acid conditions.

Trifluoroacetoxylation of the aromatic ring has been observed previously for only anthracene,[10–12] triptycene,[12] and the benzanthracenes[13] and then only with Tl(TFA)$_3$–TFAH as the oxidant. Eberson however has found EPR evidence that the 1,2,4,5,6,8-hexamethylanthracene radical cation (ArH$^{\bullet+}$), in TFAH, reacts with TFA$^-$ at low temperature to give, in equilibrium, the neutral radical ArH(TFA)$^{\bullet}$.[32] We have now found a further example of trifluoroacetoxylation in di-*tert*-butylbenzodioxole **16** (Table 1 and Fig. 9). Hyperfine coupling to the fluorine could not be observed, but the signals in **16a**$^{\bullet+}$ are broader than those in **16**$^{\bullet+}$, and a small coupling could have been lost in the line width.

We have never observed the spectra of aryl trifluoroacetate radical cations from the arenes in Hg(TFA)$_2$–TFAH, so that it appears possible to rule out their formation by the reaction between ArH$^{\bullet+}$ and TFAH, and to ascribe it to the presence of the Tl(TFA)$_3$ when Tl(TFA)$_3$–TFAH is used as the reagent. The trifluoroacetoxylation occurs in Tl(TFA)$_3$–TFAH at the position in the substrate with the largest value of *a*(H), as does mercuriation in Hg(TFA)$_2$–TFAH and it seems likely that thallideprotonation does precede trifluoroacetoxylation as shown in Scheme 2. It should be noted however that we could not observe the mercurideprotonation of **16**. Arylthallium bis(trifluoroacetates) are reported not to decompose spontaneously at room temperature and it is possible that the reductive elimination may proceed through the $ArTl(TFA)_2^{\cdot +}$ radical cation.

## Experimental

### EPR Spectroscopy

EPR Spectra were recorded on a Bruker ESP300 spectrometer operating at *ca.* 9.2 GHz, and fitted with a 500 W high pressure mercury arc provided with neutral (metal gauze, 10 and 30% transmission) and Pyrex glass filters. This is the source which is referred to in the text as filtered UV light.

Samples were prepared by introducing a solution of $Hg(TFA)_2$ or $Tl(TFA)_3$ (5 mg) in TFAH (1 $cm^3$) into a Suprasil silica tube, 3 mm id, 0.5 mm wall. The substrate (*ca.* 0.05 mg) was added, and the solution was degassed for *ca.* 2 min with a stream of nitrogen. With all the compounds, samples which were photolysed were compared with samples which had been prepared and kept in the dark for the same period.[6,12] In every case, this established that mercuration was photocatalysed.

### Substrates

Compounds **8**,[12] **10**,[17] **11**,[12] and **15**[15] have been described in our earlier papers. 2-Methylbiphenylene **9** and tribenzocyclododecatrienetriyne **18** were a gift from Dr M. Shepherd (University of North London), and benzo[1,2-*b*:4,5-*b′*]bis-1,4-dioxane **13** and benzo[1,2-*d*:3,4-*d′*]bis[1,3]dioxole **17** were provided by Professor R. Lapouyade (Bordeaux). The other compounds were prepared by methods which are described in the literature, and showed properties similar to those which have been reported.

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*Paper 8/06670A*