

# Redox and EPR Spectral Behaviour of Radical Cations of Dibenzothiophene and Some of its Derivatives

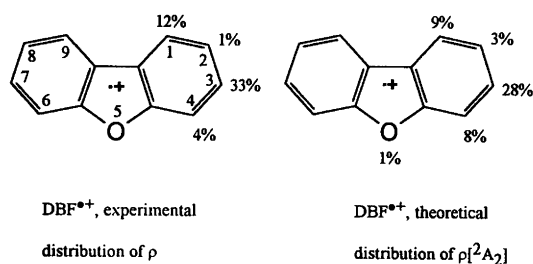
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The radical cations of dibenzothiophene **1** and its 2,8-[<sup>2</sup>H<sub>2</sub>]-isotopomer (**2**), a series of methylated dibenzothiophenes, viz. 2,8- (**3**), 3,7- (**4**) and 4,6-dimethyldibenzothiophene (**5**), and 2,4,6,8-tetramethyldibenzothiophene (**6**), as well as 2,2'- (**7**) and 4,4'-bidibenzothiophene (**8**) have been generated in 1,1,1,3,3,3-hexafluoropropan-2-ol, mostly by Tl<sup>III</sup> trifluoroacetate or 4-tolyl-Tl<sup>III</sup> trifluoroacetate oxidation. From the hyperfine coupling constants obtained, it is concluded that the 2- and 4-positions of **1**<sup>•+</sup> are the carbon atoms possessing the highest spin density. This assignment agrees with results of high-level quantum-chemical calculations, placing the <sup>2</sup>B<sub>1</sub> state as the lowest energy level of **1**<sup>•+</sup>.

It was shown recently<sup>1</sup> that the distribution of spin density ( $\rho$ ) based upon the HFS constants of the EPR spectrum of the dibenzofuran radical cation (DBF<sup>•+</sup>, below, left) was only compatible with the theoretically calculated distribution if the radical cation state of lowest energy was assumed to be <sup>2</sup>A<sub>2</sub> (below, right). For the

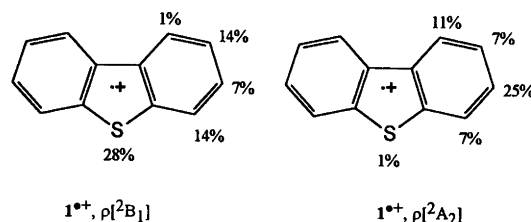


Scheme 1.

<sup>2</sup>B<sub>1</sub> state, the theoretical spin density distribution favoured the 2- and 4-positions. Since the two radical cation states were found to be nearly degenerate by high-level quantum chemical calculations, the experimental determination of EPR parameters represents one unequivocal way to decide the order between their energy levels.

For dibenzothiophene radical cation (**1**<sup>•+</sup>), similar calculations<sup>2</sup> gave the spin density distributions for the two states shown in Scheme 2. Here the ordering of the states was unequivocally calculated to be that the <sup>2</sup>B<sub>1</sub> state is the lower one in energy, the difference being as large as 0.5 eV, in good agreement

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Scheme 2.

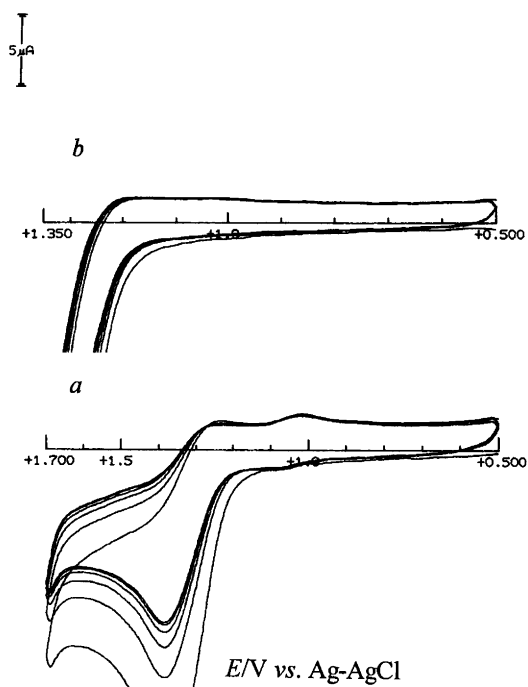
with the difference ( $\sim 0.4$  eV) between experimental values determined in the gas phase.<sup>3</sup> In order to check if the same relationship is valid for **1**<sup>•+</sup> in solution, we have recorded the EPR spectra of the radical cations of **1** and its 2,8-[<sup>2</sup>H<sub>2</sub>]-isotopomer (**2**), a series of methylated dibenzothiophenes, viz. 2,8- (**3**), 3,7- (**4**) and 4,6-dimethyldibenzothiophene (**5**) and 2,4,6,8-tetramethyldibenzothiophene (**6**), as well as 2,2'- (**7**) and 4,4'-bidibenzothiophene (**8**). From the HFS constants determined, it is inferred that the experimental spin density distribution of **1**<sup>•+</sup> is in accordance with that calculated for the <sup>2</sup>B<sub>1</sub> state.

While the EPR spectrum of the dibenzothiophene radical anion (**1**<sup>•-</sup>) has been known for a long time,<sup>4</sup> that of **1**<sup>•+</sup> has been obtained only in unresolved shape in trifluoroacetic acid at room temperature.<sup>5</sup> In this medium it was prepared by oxidation of **1** by what in all probability was the hydroquinone radical cation, formed by photolysis of 1,4-benzoquinone.<sup>6</sup> We have utilized mainly Tl<sup>III</sup> based oxidants, using either trifluoroacetic acid or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) as the

**Table 1.** Cyclic voltammetry of dibenzothiophene **1** and derivatives **3–8** in HFP-Bu<sub>4</sub>NPF<sub>6</sub> (0.15 mol dm<sup>-3</sup>), unless otherwise stated.<sup>a</sup>

Dibenzothiophene derivative	$E_{\text{rev}}/V$ vs. Ag/AgCl <sup>b</sup>	Reversibility at $v/V$ s <sup>-1</sup>	Approximate half-life of radical cation/s
Unsubstituted ( <b>1</b> )	1.26	>20	10 <sup>-2</sup>
2,8-Me <sub>2</sub> ( <b>3</b> )	1.12	0.1 <sup>c</sup>	>10
3,7-Me <sub>2</sub> ( <b>4</b> )	1.21	>10	10 <sup>-2</sup>
4,6-Me <sub>2</sub> ( <b>5</b> )	1.20	>2	10 <sup>-1</sup>
2,4,6,8-Me <sub>4</sub> ( <b>6</b> )	1.04	0.1 <sup>c</sup>	>10
2,2'-Bi- ( <b>7</b> )	1.08 <sup>d</sup>	0.1 <sup>c</sup>	>10
4,4'-Bi- ( <b>8</b> )	1.25 <sup>d</sup>	>0.2	10 <sup>0</sup>

<sup>a</sup>The anode was a Pt button of diameter 1 mm and measurements were performed at 22 °C. <sup>b</sup>In HFP,  $E_{\text{rev}}$  of ferricinium-ferrrocene = 0.05 V vs. Ag/AgCl. <sup>c</sup>This is the sweep rate used for the determination of  $E_{\text{rev}}$ ; the limit was situated at a lower sweep rate. <sup>d</sup>In HFP-dichloromethane (7:3 v:v).



**Fig. 1.** Multisweep cyclic voltammetry at  $v=1$  V s<sup>-1</sup> of dibenzothiophene (**1**) (1.3 mmol dm<sup>-3</sup>) in HFP-Bu<sub>4</sub>NPF<sub>6</sub> (0.15 mol dm<sup>-3</sup>); sweep range 0.5–1.7 V (a) or 0.5–1.35 V (b).

solvent, the latter being the preferred one.<sup>7</sup> Its combination of high polarity, low nucleophilicity and astounding capacity to suppress nucleophile reactivity makes it an ideal solvent for recording EPR spectra of radical cations.<sup>7b</sup>

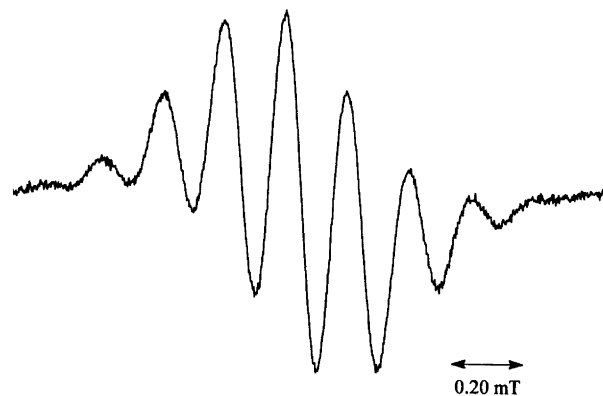
**Cyclic voltammetry of 1 and 3–8.** Table 1 gives reversible potentials for the first step of the oxidation of **1** and **3–8**, measured in HFP/Bu<sub>4</sub>NPF<sub>6</sub> (0.15 mol dm<sup>-3</sup>), in the cases of **7** and **8** admixed with 30% dichloromethane because of their low solubility in neat HFP.

For dibenzothiophene **1** ( $[1]=1.3$  mmol dm<sup>-3</sup>) reversibility became well developed in HFP at sweep rates ( $v$ )

above 20 V s<sup>-1</sup>. At sweep rates between 1 and 5 V s<sup>-1</sup>, cycling of the potential between 0.5 and 1.7 V led to the development of a second, reversible redox couple with  $E_{\text{rev}} \approx 1.04$  V (Ag/AgCl),  $i_{\text{pa}}$  being about 5% of that of the 1<sup>•+</sup>/1 couple [Fig. 1(a)]. This is approximately the same value as  $E_{\text{rev}}$  of 2,2'-bidibenzothiophene, considering the slight difference in solvents (Table 1). When the anodic potential limit was lowered incrementally, the second couple diminished in peak height until it completely disappeared when the cycling direction was switched at the anodic peak potential of DBT, 1.35 V [Fig. 1(b)]. Increasing the anodic potential limit eventually demonstrated a second, irreversible step with  $E_{\text{pa}} = 1.75$  V.

Blocking the 2,8-positions by methyl groups (**3** and **6**) strongly increased the stability of the corresponding radical cations, indicating that the 2(8)-position of 1<sup>•+</sup> is a reactive one. This was also seen from the high stability of the 2,2'-dehydrodimer radical cation (7<sup>•+</sup>). An increase in stability was also noticed for 4,6-dimethyl substitution (**5**), whereas 3,7-dimethyl substitution (**4**) had little effect.

**EPR spectra of the radical cation of dibenzothiophene 1, 2,8-[<sup>2</sup>H<sub>2</sub>]dibenzothiophene 2, 2,2'-bidibenzothiophene 7 and 4,4'-bidibenzothiophene 8.** When **1** was oxidized by thallium(III) trifluoroacetate (abbreviated Tl<sup>III</sup> in the following) in HFP a blue solution resulted from which the moderately well resolved seven-line (splitting 0.175 mT) EPR spectrum of Fig. 2 was recorded. This spectrum disappeared with an apparent half-life of about 25 min and kept its appearance during its lifetime. At the same time the blue colour faded away. The same spectrum could be recorded by UV irradiation of a solution of **1** and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in HFP–15% trifluoroacetic acid at 22 °C, the acid being added to protonate DDQ radical anion which otherwise dominated the EPR spectrum. The spectrum of Fig. 2 was also obtained from UV irradiation of **1** and mercury(II) trifluoroacetate in HFP at 22 °C or in trifluoroacetic acid at –12 °C. When the light was



**Fig. 2.** EPR spectrum recorded 10 min after mixing of a solution of dibenzothiophene **1** (6 mmol dm<sup>-3</sup>) and Tl<sup>III</sup> (ca. 10 mmol dm<sup>-3</sup>) in HFP.

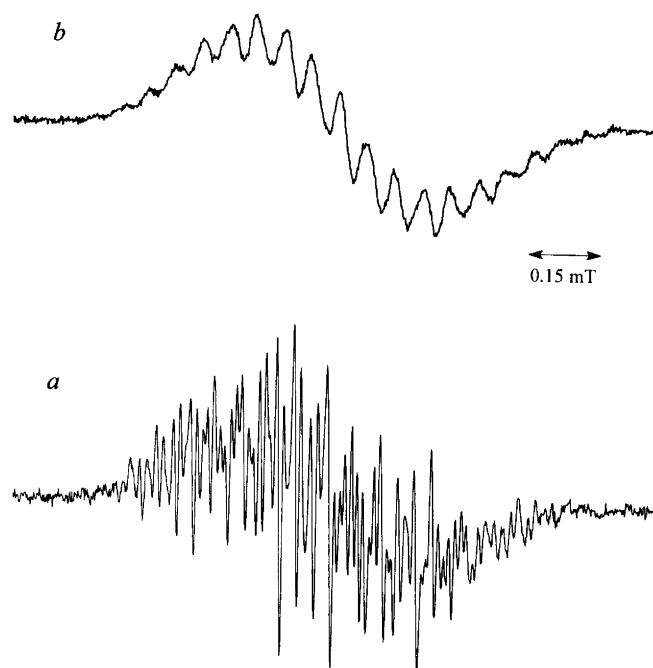


Fig. 3. EPR spectrum recorded from a solution of 2,2'-bidibenzothiophene (**7**) (satd.) and tolyl-Tl<sup>III</sup> (ca. 5 mmol dm<sup>-3</sup>) in HFP containing 3% (v:v) trifluoroacetic acid at a modulation amplitude of (a) 0.005 or (b) 0.05 mT.

switched off in the HFP experiment at 22 °C, the spectrum disappeared with a half-life of about 15 s. No further resolution of the spectrum of Fig. 2 was possible under the conditions tried.

Since the CV data indicated that **7** might possibly be formed by oxidation of **1**, the EPR spectrum of **7**<sup>•+</sup> was recorded by oxidation of a solution of **7** in HFP–3% trifluoroacetic acid by 4-tolylthallium(III) trifluoroacetate (abbreviated tolyl-Tl<sup>III</sup> in the following). The spectrum is shown at the highest resolution possible in Fig. 3(a); at higher modulation amplitude it degenerated into a multiplet with an approximate splitting of 0.06 mT [Fig. 3(b)]. The half-life of the signal was of the order of 25 h. The same spectrum was obtained by Tl<sup>III</sup> oxidation of **7** in HFP, but then it had a shorter half-life, ca. 3.5 h. Irradiation of **7**-Hg<sup>II</sup> trifluoroacetate in HFP gave a less well resolved spectrum of **7**<sup>•+</sup>; after the light had been switched off, this signal decayed with a half-life of ca. 10 min. At both high and low resolution the spectrum of **7**<sup>•+</sup> was distinctly different from the spectrum of Fig. 2, and no signal resembling that of Fig. 3(b) appeared under any of the conditions used for recording the spectrum of Fig. 2.

The 4,4'-dehydrodimer **8** gave upon oxidation by Tl<sup>III</sup> in HFP–3% trifluoroacetic acid a moderately well resolved spectrum of seven lines with an approximate 0.22 mT splitting.

The oxidation of 2,8-[<sup>2</sup>H<sub>2</sub>]dibenzothiophene **2** by Tl<sup>III</sup> in HFP gave a spectrum (Fig. 4) where a quintet splitting of 0.030 mT to two deuterium atoms showed that the HFS coupling constant to the 2(8)-H is 0.030 × 6.5 =

0.195 mT. In addition two coupling constants of 0.14 and 0.185 G, each to 2 H, were discernible.

*EPR spectra of the radical cations of 2,8-dimethyl- (3) and 2,4,6,8-tetramethyldibenzothiophene (6).* Both **3** and **6** gave persistent radical cations upon oxidation by tolyl-Tl<sup>III</sup> or Tl<sup>III</sup> in HFP or HFP–3% trifluoroacetic acid from which well resolved EPR spectra (Figs. 5 and 6) were obtained. In the **3**<sup>•+</sup> spectrum, the largest coupling constant is to the six methyl hydrogens in the 2(8)-position, and by analogy the largest coupling constant is assigned to the same position in **6**<sup>•+</sup>. The second largest coupling constant in the spectrum of **6**<sup>•+</sup> is to the methyls of the 4(6)-positions, suggesting that the second largest coupling in the spectrum of **3**<sup>•+</sup> should be assigned to the 4(6)-hydrogens. The remaining coupling constants are assigned in descending order to the 3(7) and 1(9)-positions (see Discussion).

*EPR spectrum obtained from the oxidation of 3,7-dimethyldibenzothiophene 4.* The CV behaviour of **4** indicated low stability of its radical cation. When **4** was oxidized by tolyl-Tl<sup>III</sup> in HFP–6% trifluoroacetic acid, the EPR spectrum was a broad unresolved singlet ( $\Delta H_{pp}$  about 0.5 mT); with Tl<sup>III</sup> as the oxidant in the same medium, a much wider, resolved EPR spectrum could be recorded. It appeared to be a superposition of two spectra (Fig. 7), the more intense of which could be analyzed in terms of  $a^H = 0.868$  (6 H), 0.252 (2 H), 0.012 (6 H) and 0.008 (2 H) mT. We assign this spectrum to the radical cation of the 2,2'-coupled dimer **9**; the fact that a small coupling to a second set of six hydrogens could be resolved shows that a dimer structure must be

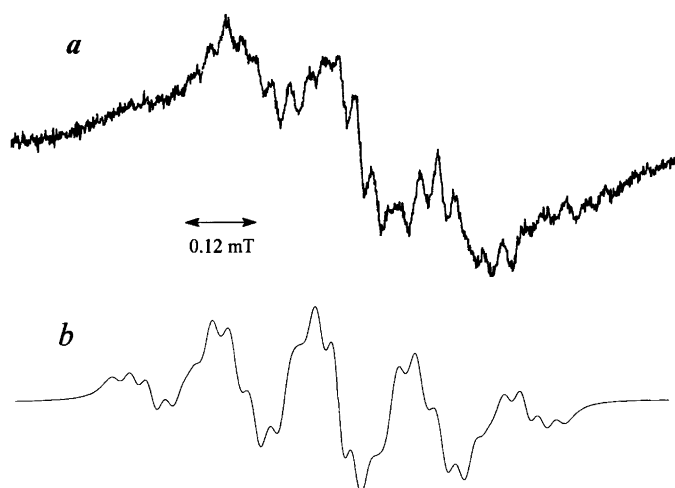


Fig. 4. (a) EPR spectrum recorded 10 min after mixing of a solution of 2,8- $[\text{2H}_2]$ dibenzothiophene (**2**) ( $6 \text{ mmol dm}^{-3}$ ) and  $\text{Tl}^{\text{III}}$  (ca.  $10 \text{ mmol dm}^{-3}$ ) in HFP. (b) Simulated spectrum using  $a^{\text{D}}$  (2 D) =  $0.195/6.5 = 0.030 \text{ mT}$ ,  $a^{\text{H}}$  (2 H) =  $0.185 \text{ mT}$  and  $a^{\text{H}}$  (2 H) =  $0.142 \text{ mT}$ , lorentzian lineshape and linewidth  $0.025 \text{ mT}$ .

involved. Also its relatively long half-life, ca. 30 min, is in accord with a dimeric structure.

*EPR spectrum of the radical cation of 4,6-dimethyl-dibenzothiophene (5).* Oxidation of **5** by  $\text{Tl}^{\text{III}}$  in HFP gave a strong 11-line spectrum with a splitting of  $0.17 \text{ mT}$  (Fig. 8). The spectral pattern is compatible with  $a^{\text{H}} = 0.17$  (6 H) and  $0.35$  (2 H) mT, no other coupling constants being larger than  $0.05 \text{ mT}$ .

## Discussion

*Dibenzothiophene radical cation ( $\text{1}^{\cdot+}$ ).* The fact that the  $\text{1}^{\cdot+}/\text{1}$  couple becomes reversible in HFP only at sweep

rates above  $20 \text{ V s}^{-1}$  ( $E^\circ = 1.26 \text{ V vs. Ag/AgCl}$ ) indicates a short half-life of  $\text{1}^{\cdot+}$ , of the order of  $0.03 \text{ s}$ . No sign of oligomerization was seen when the direction of the potential sweep was reversed at the anodic peak potential [Fig. 1(b)]. If the reversal was performed at a higher potential, at least  $0.15 \text{ V} > E_{\text{pa}}$ , a second couple with  $E^\circ \approx 1.04 \text{ V}$  appeared, in all probability due to the 2,2'-bidibenzothiophene system,  $\text{7}^{\cdot+}/\text{7}$ . Since the latter appears only after sweep reversal at higher potentials, it is assumed to be a product of further reaction of the dication,  $\text{1}^{2+}$ . The preparative anodic oxidation of **1** in acetonitrile– $\text{NaClO}_4$  ( $0.1 \text{ M}$ ) at the potential of the first irreversible step,  $1.25 \text{ V vs. Ag/Ag}^+$  ( $0.1 \text{ mol dm}^{-3}$ ), has been shown<sup>8</sup> to give a sulfonium salt, suggested to be

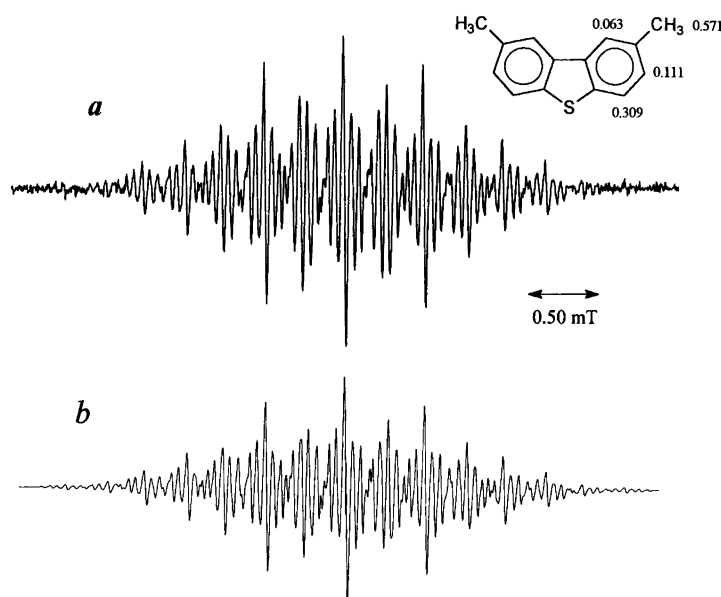


Fig. 5. (a) EPR spectrum recorded from a solution of 2,8-dimethyldibenzothiophene (**3**) (satd.) and  $\text{Tl}^{\text{III}}$  (ca.  $10 \text{ mmol dm}^{-3}$ ) in HFP containing 3% (v:v) trifluoroacetic acid. (b) Simulated spectrum using the coupling constants shown in the figure, lorentzian lineshape and linewidth  $0.020 \text{ mT}$ .

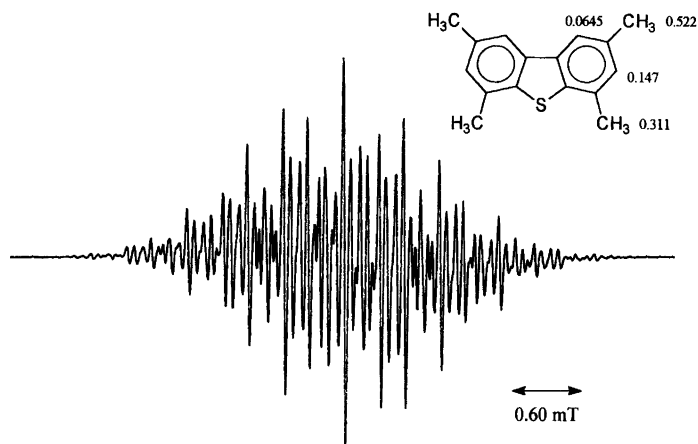


Fig. 6. EPR spectrum recorded from a solution of 2,4,6,8-tetramethyldibenzothiophene (**6**) (satd.) and  $Tl^{III}$  (ca.  $10 \text{ mmol dm}^{-3}$ ) in HFP containing 3% (v:v) trifluoroacetic acid.

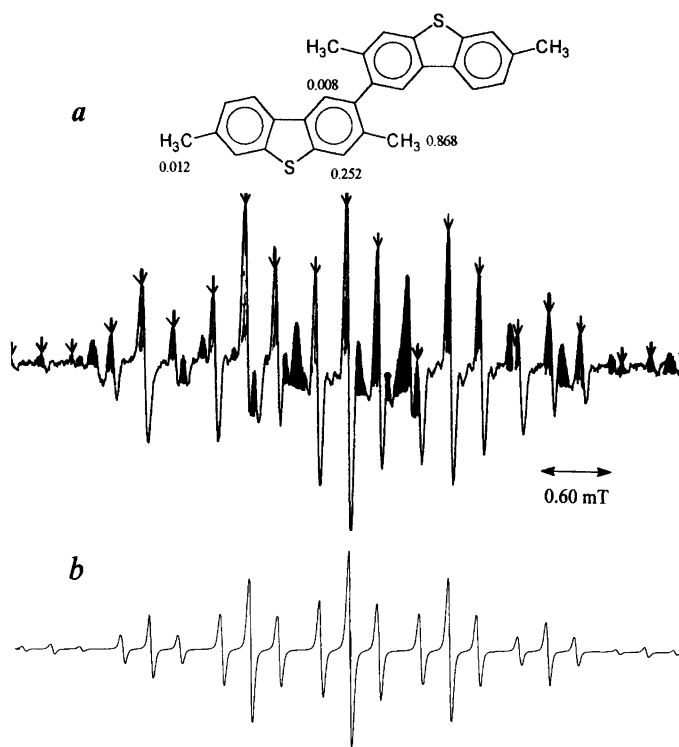


Fig. 7. (a) EPR spectrum recorded from a solution of 3,7-dimethyldibenzothiophene (**4**) (satd.) and  $Tl^{III}$  (ca.  $10 \text{ mmol dm}^{-3}$ ) in HFP containing 6% (v:v) trifluoroacetic acid. The spectrum assigned to (**9**) is marked by arrows. (b) Simulated spectrum for the coupling constants given in the figure, lorentzian lineshape and linewidth 0.020 mT.

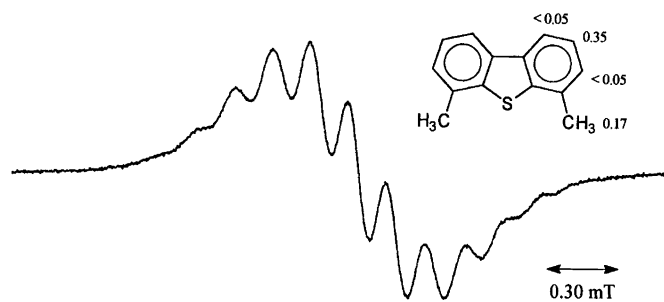
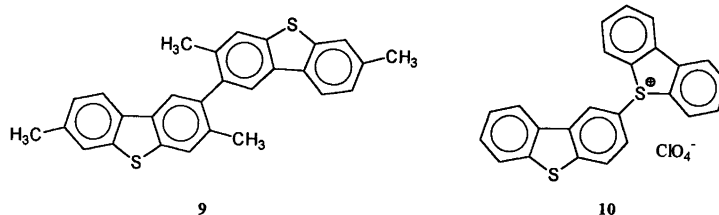


Fig. 8. EPR spectrum recorded from a solution of 4,6-dimethyldibenzothiophene (**5**) (satd.) and  $Tl^{III}$  (ca.  $10 \text{ mmol dm}^{-3}$ ) in HFP.



Scheme 3.

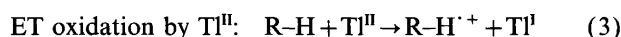
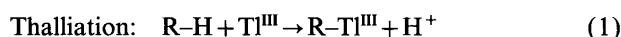
the *S*,2'-connected species **10**, as the single product. The connectivity was not fully proven, however. The further oxidation of **10** took place at a potential ca. 0.3 V above the potential of **1**.

The anodic behaviour of the  $1^{\cdot+}/1$  couple raises the problem of the identity of the species corresponding to the seven-line spectrum of Fig. 2. This species had a half-life of 25 min in HFP at 22 °C when generated by  $Tl^{III}$  oxidation of **1** and ca. 15 s when generated in homogeneous solution by photolysis of **1** in the presence of  $Hg^{II}$  trifluoroacetate. Similar behaviour was noted for the dehydrodimer **7**: the 'half-lives' of its radical cation after generation by  $Tl^{III}$ , tolyl- $Tl^{III}$  or  $Hg^{II}-h\nu$  oxidation in HFP were 1500, 210 or 10 min, respectively.

This type of kinetic behaviour is similar to that of the hexamethylbenzene (HMB) system.<sup>9</sup> Oxidation of HMB by  $Tl^{III}$  in trifluoroacetic acid at 22 °C gave  $HMB^{\cdot+}$  with an apparent half-life of ca. 40 s, whereas  $HMB^{\cdot+}$  generated by  $Hg^{II}-h\nu$  or anodic oxidation of HMB under the same conditions decayed with a half-life of 1–1.5 s; at –11 °C, the corresponding half-lives were 28 and ca. 0.1 min. This anomaly was resolved by the assumption that  $Tl^{III}$  oxidation of aromatic compounds to give the corresponding radical cations is not of simple outer-sphere character but instead follows a complex mechanism involving several steps. This means the initial step of  $Tl^{III}$  oxidation of HMB is a *slow* reaction, in all probability involving a thallation mechanism, the rate of which determines the apparent slow decay of  $HMB^{\cdot+}$  generated in this way. Kinetic simulations show that such a scheme produces a low, but stable and long-lasting concentration of  $HMB^{\cdot+}$  the EPR spectrum of which can be conveniently monitored.<sup>7b</sup> On the other hand, with a rapidly reacting oxidant a high concentration of the radical cation is momentarily formed, but it decays too fast for any measurement to be possible. Under photolytic conditions, a stationary concentration of the radical cation is established; when irradiation is interrupted the radical cation decays according to its 'normal' rate behaviour.

A mechanism involving slow thallation as the initial step would account for the favourable properties of  $Tl^{III}$  based reagents for the generation of radical cations. So far it has been documented<sup>9</sup> kinetically only for HMB which would then entail thallation at a benzylic position. Since thallation at nuclear positions of  $ArH$  is a reaction of wide scope and utility,<sup>10</sup> we suggest that a thallation step and/or the subsequent homolytic cleavage of the

organothallium intermediate in general is the slow step in the generation of radical cations, as shown in eqns. (1) and (2). In this way, the strong ET oxidant  $Tl^{II}$  is formed ( $E^\circ[Tl^{II}/Tl^I]$  is about 2.2 V while  $E^\circ[Tl^{III}/Tl^{II}]$  only is 0.3 V),<sup>11</sup> and a second molecule of  $R-H$  can be oxidized in a fast step [eqn. (3)].

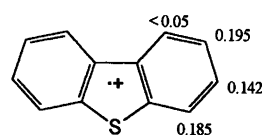


$R = Ar, ArCH_2$

Table 2 lists reversible potentials in HFP for some aromatic systems, the primary radical cations of which have been monitored EPR spectroscopically after oxidation by  $Tl^{III}$ . The range of potentials is 1.17–1.84 V vs.  $Ag/AgCl$ , corresponding to 1.14–2.1 V on the scale of the NHE. The systems chosen thus correspond to reactive radical cations which yet appear EPR spectroscopically as 'stable' species due to the mechanism of formation of eqns. (1)–(3). In such a context, there is nothing inherently implausible with the apparent half-life of  $1^{\cdot+}$  of 28 min.

Thus we conclude that the primary radical cation  $1^{\cdot+}$  is monitored EPR spectroscopically from the oxidation of **1** by  $Tl^{III}$  under the conditions reported above. The EPR spectrum of the authentic 2,2'-dehydrodimer, the most likely product of carbon-to-carbon coupling of  $1^{\cdot+}$  and oxidized at a potential ca. 0.2 V lower than that of the 4,4'-isomer, appears in well resolved form and collapses to a multiplet with a splitting of about 0.060 mT at lower resolution (Fig. 3). The spectrum is also much more persistent than that of  $1^{\cdot+}$ . The sulfonium ion **10**, the most probable product of *S*-to-*C* coupling of two  $1^{\cdot+}$ , is not expected to be oxidized in the presence of **1** in view of its ca. 0.3 V higher oxidation potential.<sup>8</sup>

From the information gained by the EPR spectra of  $1^{\cdot+}$  and its 2,8-bisdeuteriated form, the following HFS constants (in mT) can be assigned:



Scheme 4.

Table 2.  $E^\circ(\text{ArH}^+/\text{ArH})$  of some ArH, measured in HFP-Bu<sub>4</sub>NPF<sub>6</sub> (0.15 mol dm<sup>-3</sup>), and the apparent half-lives of their primary radical cations when generated by Tl<sup>III</sup> trifluoroacetate oxidation of ArH in HFP.

Aromatic system	$E^\circ(\text{ArH}^+/\text{ArH})/\text{V}$ vs. Ag/AgCl in HFP (at sweep rate $> 1/\text{V s}^{-1}$ )	Half-life of EPR signal of ArH <sup>•+</sup> /min	Ref.
Hexamethylbenzene	1.17(1)	4	7a
4,4'-Bitoluene	1.25(0.1)	66	7a
Phenanthrene	1.28(5)	≈ 2	7a
4-Fluoroanisole	1.45(2)	≈ 10	7a,18
Triptycene	1.56(50)	≈ 2	7a
4,4'-Difluorobiphenyl	1.53(0.1)	≈ 100	7a,19
1,4-Difluoronaphthalene	1.49(0.1)	230	7a,19
2,3,5,6-Tetrafluoro-4-methylanisole	1.84(2)	≈ 5	19
Dibenzothiophene (010)	1.26(20)	28	This work

This indicates that the electronic structure of  $1^{\bullet+}$  is that calculated for the  ${}^2\text{B}_1$  state, where relatively little spin density is delocalized to mainly the 2(8)- and 4(6)-ring positions, the main part residing on sulfur (see Scheme 2). This agrees with the chemical properties of  $1^{\bullet+}$  as being much less prone to undergo C-to-C dimerization than the dibenzofuran radical cation, its  ${}^2\text{A}_2$  state possessing high spin density in the 3(7)-positions as evidenced by the much larger HFS constant of 0.7 mT. The latter radical cation could not be observed by EPR spectroscopy in fluid solution and underwent electropolymerization in both HFP and DCM.<sup>1</sup>

*2,8-Dimethyl- (3) and 2,4,6,8-tetramethyldibenzothiophene (6) radical cations.* The assignment of HFS constants in the spectra of the persistent radical cations  $3^{\bullet+}$  and  $6^{\bullet+}$  is shown in Figs. 5 and 6. In the spectrum of  $3^{\bullet+}$ , the seven-line splitting of the 2(8)-methyl groups clearly identifies the large  $a^{\text{H}}$  of 0.571 mT, showing that spin density is effectively delocalized into the methyl groups. The large  $a^{\text{H}}$  of the  $6^{\bullet+}$  spectrum is assigned by analogy, which then fixes the  $a^{\text{H}}$  of the 4(6)-methyl groups at 0.311 mT. Again by analogy, the 0.309 mT coupling in  $3^{\bullet+}$  is then assigned to the 4(6) ring hydrogens. The smallest coupling constant of ca. 0.06 mT in both spectra is assigned to the 1(9)-positions on the basis of the quantum chemical calculations (see Scheme 2).

*4,6-Dimethyldibenzothiophene (5) radical cation.* This radical cation gave a moderately well resolved spectrum, with coupling constants assigned according to Fig. 8.

*3,7-Dimethyldibenzothiophene (4) radical cation and its dimer.* It is likely that the broad singlet spectrum obtained by oxidation of **4** by tolyl-Tl<sup>III</sup> should be assigned to the primary radical cation  $4^{\bullet+}$ . The tolyl-Tl<sup>III</sup> reagent is less reactive than Tl<sup>III</sup> and does not sustain further transformations of the initially formed radical cation, such as trifluoroacetoxylation, coupling and cyclization, as Tl<sup>III</sup> does.<sup>7a</sup> The spectrum obtained by Tl<sup>III</sup> oxidation of **4** must be assigned to a dimeric structure, most probably the 2,2'-dehydrodimer **9**, since two couplings each have the multiplicity for six hydrogens.

*Comparison between the dibenzofuran and dibenzothiophene systems.* As summarized in Table 3, radical cations of dibenzofuran are stabilized by attaching methyl substituents to the reactive 1(9)- and/or 3(7)-positions, as judged by the reversible potentials and the persistency of the radical cations.<sup>1</sup> Methyl groups in the 2(8)- and/or 4(6)-positions have little effect upon the stability, and in fact 2,8-dimethyldibenzofuran is oxidized to its 3,3'-connected dehydrodimer by Tl<sup>III</sup>. This is in accord with the spin density distribution of the  ${}^2\text{A}_2$  state, with high  $\rho$ -values particularly in the 3(7)-positions but also in the 1(9)-positions.

The behaviour of methylated dibenzothiophenes is analogous (Table 3), except that the reactive loci are now the 2(8)- and 4(6)-positions. Thus higher stability is imparted by methyl groups in these positions, and 3,7-dimethyldibenzothiophene is readily transformed into the 2,2'-connected dehydrodimer **9**.

*Comparison between the dibenzothiophene radical cation and anion.* The pairing theorem<sup>12</sup> states that the HFS constants of the ring protons in a radical cation derived from an alternant aromatic system should be equal or nearly equal to those of the corresponding radical anion. Thus the total spectral width of the EPR spectra of the two types of ions should be equal, or, expressed differently, the ratio of the spectral widths of radical cations and anions, respectively, should theoretically be 1. For a series of alternant ArH, the ratio was shown<sup>13</sup> to be 1.09(5).

For non-alternant systems, the pairing theorem is not valid. Thus the above ratio was found to vary by more than an order of magnitude (from 0.41 to 5.13) for a number of nonalternant hydrocarbons.<sup>13</sup> Table 4 shows that the ratio is  $< 0.48$  for dibenzothiophene, and 0.86 and 0.61 for the 2,8- and 4,6-dimethyl derivatives. In the latter cases, the coupling constant to the methyl groups was taken to be equal to that of the ring hydrogen in that position. It should also be noticed that low HFS constants in the radical cations correspond to high values in the anion, and *vice versa*.

## Experimental

*Materials.* Dibenzothiophene (**1**, EGA-Chemie, 96%) and dibenzothiophene-5,5-dioxide (Aldrich, 98%) were

Table 3. Comparison of radical cation properties between dibenzofuran and dibenzothiophene derivatives.

Substituents	Dibenzofurans				Dibenzothiophenes			
	$E^\circ/V$ vs. Ag/AgCl in HFP	At $v >$ /V s $^{-1}$	EPR spectrum		$E^\circ/V$ vs. Ag/AgCl in HFP	At $v >$ /V s $^{-1}$	EPR spectrum	
			$a^{H3,7}$	$a^{H1,9}$			$a^{H2,8}$	$a^{H4,6}$
None	1.51	40	0.7	0.2–0.3	1.26	20	0.195	0.185
2,8-Me $_2$	1.32	5	Dehydrodimer		1.12	0.1	0.571 <sup>a</sup>	0.309
3,7-Me $_2$	1.18	0.1	0.90	0.212	1.21	10	Dehydrodimer	
4,6-Me $_2$	1.34	10	Broad singlet		1.20	2	0.35	0.17 <sup>a</sup>
2,4,6,8-Me $_4$	1.19	5	Broad singlet		1.04	0.1	0.522 <sup>a</sup>	0.311 <sup>a</sup>

<sup>a</sup> Coupling to methyl groups.

Table 4. HFS constants of radical cations and radical anions of dibenzo-thiophene and two dimethyl derivatives and the ratios of the overall spectral ranges.

Substituent	Position	$(a^H)^{\cdot+}/mT$	$(a^H)^{\cdot-}/mT$	$\Sigma(a^H)^{\cdot+}/\Sigma(a^H)^{\cdot-}$
None	1,9	<0.05	0.452	
	2,8	0.195	0.097	
	3,7	0.142	0.504	
	4,6	0.185	0.145	<0.48
2,8-Me $_2$	1,9	0.063	0.46	
	2,8 <sup>a</sup>	0.571	0.108	
	3,7	0.111	0.51	
	4,6	0.309	0.155	0.86
4,6-Me $_2$	1,9	<0.05	0.41	
	2,8	0.35	<0.010	
	3,7	<0.05	0.519	
	4,6 <sup>a</sup>	0.17	0.080	0.61

<sup>a</sup> For coupling to methyl groups.

used as received for syntheses. All lithiations were carried out in dry diethyl ether under argon with 2.5 mol dm $^{-3}$  butyllithium in hexane as the lithiating agent. 2,8-Dibromodibenzothiophene (**11**) was obtained by treatment of **1** with bromine in acetic acid.<sup>14</sup> 3,7-Dibromodibenzothiophene (**12**) was prepared by bromination of dibenzothiophene-5,5-dioxide<sup>15</sup> and subsequent reduction by LiAlH $_4$  (Ref. 4a). 2,8-, 3,7- and 4,6-Dimethyldibenzothiophene (**3–5**) were prepared via dilithiation of **11**,<sup>4a</sup> **12**,<sup>4a</sup> and **1**,<sup>16</sup> respectively, followed by quenching with methyl iodide. 2,4,6,8-Tetramethyldibenzothiophene (**6**) was prepared by dilithiation of **3**, followed by quenching with methyl iodide, m.p. 136–139 °C,  $^1H$  NMR (CDCl $_3$ ):  $\delta$  7.78 (s, 2 H); 7.10 (s, 2 H); 2.56 (s, 6 H); 2.51 (s, 6 H). MS: found  $M^+$  240.0973, C $_{16}$ H $_{16}$ S requires 240.0973. Compound **2** was prepared by treatment of 2,8-dibromodibenzothiophene with butyllithium, followed by quenching with deuterium oxide. Its deuterium contents was >99% (MS). All EPR spectroscopic substrates were purified on the Chromatotron as previously described for the corresponding dibenzofuran derivatives.<sup>1</sup>

2,2'-Bidibenzothiophene (**7**) was obtained from an Ullman coupling of 2-iododibenzothiophene. The compound was isolated by chromatography on a silica gel

Chromatotron plate using hexane as eluent. Evaporation of the solvent gave white crystals. m.p. 168–172 °C.  $^1H$  NMR (CDCl $_3$ ):  $\delta$  8.46 (dd, 1 H,  $J=1.9$ , 0.6 Hz), 8.29 (ddd, 1 H,  $J=6.9$ , 2.3, 0.6 Hz), 7.98 (dd, 1 H,  $J=8.3$ , 0.6 Hz), 7.90 (ddd, 1 H,  $J=6.9$ , 2.3, 0.6 Hz), 7.82 (dd, 1 H,  $J=8.3$ , 1.9 Hz), 7.5 (m, 2 H).

4,4'-Bidibenzothiophene (**8**). To a solution of 1.0 g (5.4 mmol) dibenzothiophene in 20 ml THF was added 6 mmol of butyllithium. The solution was stirred at room temperature for 2 h, and then 5 g (14 mmol) iron(III) acetylacetonate was added. The mixture was stirred for 1 h and then poured into 200 ml of 10% hydrochloric acid. Extraction with 100 ml of dichloromethane/pentane (1/5, v/v) and repeated washings with 100 ml 10% hydrochloric acid gave an almost colourless extract. Drying with MgSO $_4$ , evaporation of the solvent and recrystallization from acetic acid gave pure 4,4'-bidibenzothiophene. m.p. 189–193 °C (litt.<sup>17</sup> 189–190 °C).  $^1H$  NMR (CDCl $_3$ ):  $\delta$  8.26 (dd,  $J=7.9$ , 1.2 Hz), 8.23 (ddd,  $J=7.2$ , 7.2, 1.5 Hz), 7.79 (ddd,  $J=7.2$ , 7.2, 1.5 Hz), 7.75 (dd,  $J=7.3$ , 1.2 Hz), 7.63 (dd,  $J=7.9$ , 7.3 Hz), 7.49 (ddd,  $J=7.2$ , 1.5, 0.6 Hz), 7.45 (ddd,  $J=7.2$ , 1.5, 0.6 Hz).

**Methods.** Cyclic voltammetry and EPR spectroscopic measurements were made as described before.<sup>1</sup> All EPR spectra were well simulated by the HFS constants and multiplicities given above (WIN-EPR software from Bruker AG).

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