PERKIN 2

EPR spectra and redox properties of radical cations of dibenzofuran, methylated dibenzofurans and bidibenzofurans: relation to the chemistry of dibenzofuran radical cation

Lennart Eberson,[*,a] **Michael P. Hartshorn,**[b] **Ola Persson,**[a] **Finn Radner**[a] **and Christopher J. Rhodes**[c]

[a] *Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden*
[b] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*
[c] *School of Chemical and Physical Sciences, John Moores University, Byrom Street, Liverpool, UK L3 3AF*

The radical cations of dibenzofuran 1, a variety of symmetrically methylated dibenzofurans, *viz*. 1,9- 2, 2,8- 3, 3,7- 4 and 4,6-dimethyldibenzofuran 5, 2,4,6,8- 6 and 1,3,7,9-tetramethyldibenzofuran 7, 1,3,4,6,7,9-hexamethyl- 8 and octamethyl-dibenzofuran 9, the three symmetrical dehydrodimers, 2,2′- 10, 3,3′- 11 and 4,4′-bidibenzofuran 12 and the unsymmetrical dehydrodimer 2,3′-bidibenzofuran 13 have been studied by cyclic voltammetry and EPR spectroscopy. For the latter purpose, the radical cations were generated by oxidation with thallium(III) trifluoroacetate in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 22 °C or by DDQ-light oxidation in trifluoroacetic acid at − 12 °C. For the dibenzofuran radical cation and its 2-deuteriated isotopomer, a matrix study was performed in $CFCl_3$ at − 196 °C.

The dibenzofuran radical cation could not be generated in fluid solution due to its high reactivity, leading to the formation of oligomeric and polymeric species. Monomeric compounds 4, 7, 8 and 9, which have the 3,7-positions blocked for further reaction, gave persistent monomeric radical cations, whereas the remaining ones underwent fast transformations to other species ($\mathbf{3}^{\bullet +}$ to a dehydrodimer radical cation, $\mathbf{2}^{\bullet +}$, $\mathbf{4}^{\bullet +}$–$\mathbf{6}^{\bullet +}$ to oligomeric species). An analysis of the hfs constants of the monomeric radical cations indicated that the 3,7-positions of $\mathbf{1}^{\bullet +}$ carry about 70% of the total spin density which is in agreement with the so far known chemistry of this nonalternant radical cation.

Both dehydrodimers 10 and 11 gave fairly persistent radical cations, whereas that of 12 could not be detected, presumably due to oligomerization. The radical cation of the 2,3′-dehydrodimer gave an EPR spectrum showing that the spin density is localized on one of the dibenzofuran moieties.

Electrophilic reagents generally attack dibenzofuran [**1**; numbering system, see Fig. 1(*a*)] predominantly at the 2-position.[1] Nitration was long considered to be an exception, leading to predominant formation of the 3-nitro derivative.[2] However, it was recently proposed and demonstrated[3a] that nitration at the 3-position of **1** is a consequence of the operation of the nitrous acid catalysed pathway, shown[4] to have the radical cation of the substrate as the critical intermediate [eqns. (1)–(4)].

$$HNO_2 + H^+ \longrightarrow H_2O + NO^+ \qquad (1)$$

$$ArH + NO^+ \longrightarrow ArH^{\bullet +} + NO \qquad (2)$$

$$ArH^{\bullet +} + NO_2 \longrightarrow Ar\text{–}NO_2 + H^+ \qquad (3)$$

$$(NO_2^+ + NO \longrightarrow NO_2 + NO^+) \qquad (4)$$

According to *ab initio* calculations, the spin density of $\mathbf{1}^{\bullet +}$ has its highest value at the 3-position [Fig. 1(*b*)] thus explaining the propensity of coupling with NO_2 at this position.

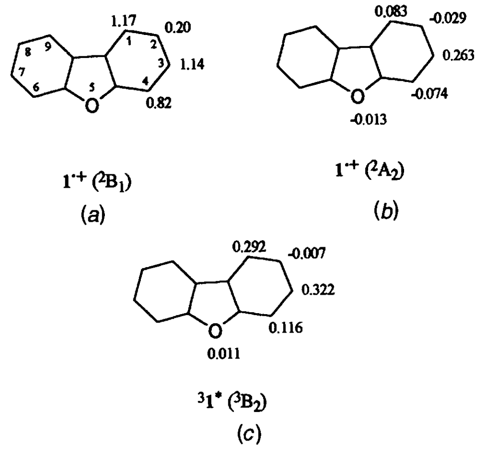


Fig. 1 (*a*) LUMO coefficients of the lowest state ($^2A_2$) of the dibenzofuran radical cation ($\mathbf{1}^{\bullet +}$), (*b*) spin density distribution in the $^2A_2$ state of $\mathbf{1}^{\bullet +}$ and (*c*) spin density distribution in the lowest dibenzofuran triplet ($^3B_2$). The IUPAC numbering system is shown in (*a*).

On the other hand, nucleophiles, such as acetate,[5] cyanide[6] and trinitromethanide ion[3] also attack $\mathbf{1}^{\bullet +}$ mainly at the 3-position, thus providing a tool for the testing of the Pross–Shaik CM model.[7] This treatment predicts that the position of attack should be decided by the LUMO coefficient of the radical cation [Fig. 1(*a*)] and the spin density of the corresponding triplet [Fig. 1(*c*)] according to the valence bond model of the transition state shown in eqn. (5).

$$Nu\!:^- \; ArH^{\bullet +} \rightleftharpoons Nu^{\bullet} \; ^3[\bullet ArH^{\bullet}]^* \qquad (5)$$

As seen from the LUMO coefficients depicted for the lowest radical cation state [$^2B_1$, Fig. 1(*a*)] and the spin densities for the lowest triplet state [$^3B_2$, Fig. 1(*c*)], the reactivity order of the positions of $\mathbf{1}^{\bullet +}$ against nucleophiles is predicted to be 3- > 1- > 2- ≈ 4-, in agreement with experimental observations. The calculations also indicated that dibenzofuran radical cation should be an easily polarizable species, an electric field of 0.01 au being sufficient to concentrate almost all the charge and spin density in one of the benzene rings. In view of the critical importance of the properties of $1^{\cdot+}$ for the reasoning referred to above, it was of importance to confirm the calculated spin density distribution by an experimental determination. Below we describe the electrochemical and EPR spectroscopic properties of the radical cations of dibenzofuran itself and a series of methylated dibenzofurans. It is shown that the 3-position of $1^{\cdot+}$ carries about 70% of the combined spin density of positions 1–4 which accounts well for its known chemistry.

Substrates

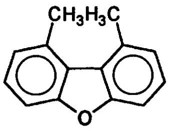
Since the dibenzofuran radical cation turned out to be a very reactive species which could not be studied by EPR spectroscopy in fluid solution, we included the four symmetrical dimethyldibenzofurans (**2**–**5**), the tetramethyl derivatives **6** and **7**, the hexamethyl compound **8** and octamethyldibenzofuran **9** in the study. The preparation of compounds **2**–**9** was recently described.[8] 2,2′-, 3,3′-, 4,4′- and 2,3′-bidibenzofuran **10**–**13** were also included in view of the possibility of dehydrodimer formation under the oxidative conditions employed.[9]

Cyclic voltammetry of compounds 1–13

In dichloromethane–tetrabutylammonium hexafluorophosphate, dibenzofuran **1**, 1,9- **2**, 2,8- **3** and 4,6-dimethyldibenzofuran **5** and 2,4,6,8-tetramethyldibenzofuran **6** at a concentration level of around 1 mmol dm^{-3} exhibited irreversible behaviour upon anodic oxidation up to a sweep rate (v) of 50 V s^{-1} (technical limit of the instrument). Repetitive scans indicated film formation due to nonconducting oligomeric material, the anodic peak current of the monomer decreasing by >90% over five cycles. On the other hand, reversible behaviour was observed at sweep rates below the upper limit in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP)[10] with tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Table 1). Methyl substitution at the 3,7-positions (compound **4**) imparted a higher kinetic stability to the radical cation so that the $4/4^{\cdot+}$ redox couple was reversible at $v > 5$ V s^{-1} even in dichloromethane. The remaining more highly substituted compounds **7**–**9**, also 3,7-dimethyl substituted, corresponded to highly stabilized radical cations.

Dibenzofuran has been reported to form a conducting polymer upon anodic oxidation,[11] and it was therefore of interest to study the effect of using the exceptionally non-nucleophilic solvent HFP[10] as a medium for this type of process. Repetitive cycling of a solution of **1** (6 mmol dm^{-3}) in HFP–tetrabutylammonium hexafluorophosphate demonstrated the build-up of a conducting film [Fig. 2(*a*)] which remained at the electrode surface for at least 30 min, as analysed by cyclic voltammetry. The material had a light yellow-brown colour and had to be removed by polishing. In a dichloromethane solution of similar composition, the same treatment led to the formation of a black film in a process with quite different electrochemical characteristics [Fig. 2(*b*)].

The two dehydrodimers **10** and **11** behaved in a similar manner upon CV. Compound **10** showed a reversible redox couple at 1.54 V in dichloromethane and at 1.11 V in HFP, both at $v = 0.1$ V s^{-1}, and **11** at 1.54 V in dichloromethane and 1.17 V in HFP–dichloromethane (1:1, v:v; **11** was too insoluble in HFP for reliable measurements to be feasible). Repeated cycling did not show any indication of polymer formation in either solvent. The 4,4′-coupled isomer, **12**, gave an irreversible anodic peak at 1.37 V in HFP (up to 50 V s^{-1}). Repeated cycling (0.1 V s^{-1}) between 0.5 and 1.45 V showed the slow buildup of a conducting film which remained at the electrode surface for at least 15 min. The 2,3′-connected isomer, **13**, showed a reversible couple at 1.15 V in HFP–dichloromethane (3:1, v:v; **13** was too insoluble in HFP for reliable measurements to be feasible) and at 1.56 V in dichloromethane.



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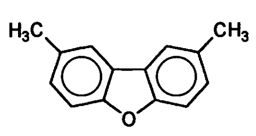

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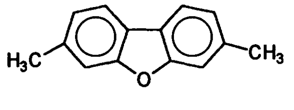

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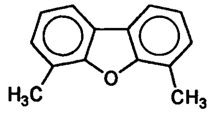

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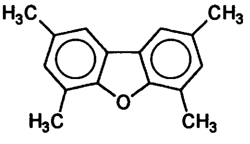

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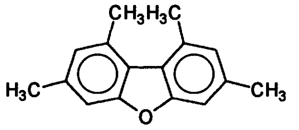

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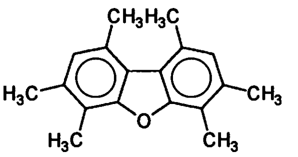

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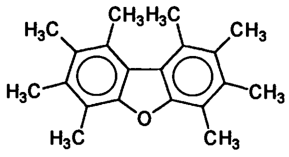

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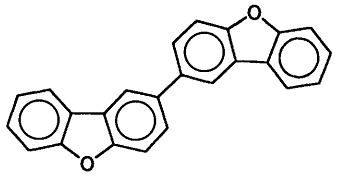

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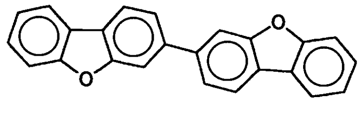

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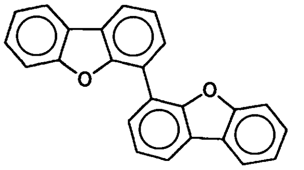

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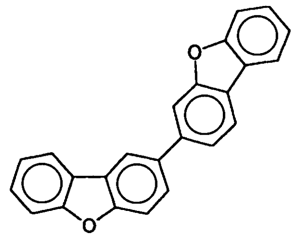

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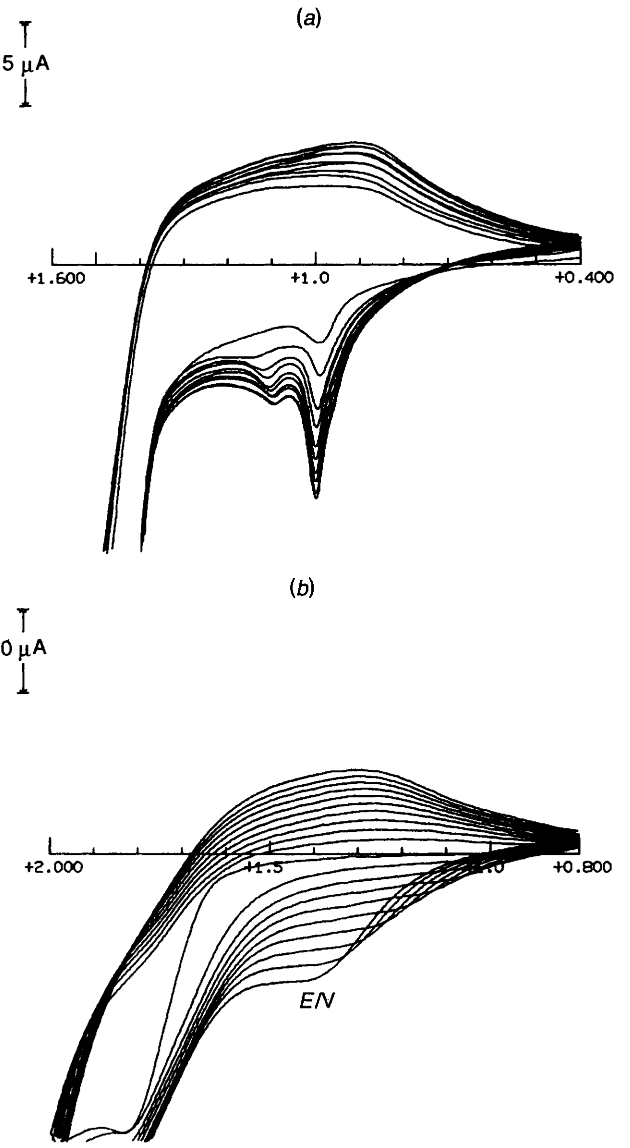


Fig. 2 Repeated electrochemical cycling (Pt anode) of a solution of dibenzofuran (6 mmol dm^{-3}) in (*a*) HFP- and (*b*) dichloromethane-Bu_4NPF_6 (0.15 mol dm^{-3}) at a sweep rate of 0.1 V s^{-1}

EPR spectroscopy of radical cations $1^{\bullet+}$–$13^{\bullet+}$

The EPR spectrum of the dibenzofuran radical cation was recorded at 77 K in a $CFCl_3$ matrix[12] and is shown in Fig. 3. If instead 2-[^{2}H] dibenzofuran was used, the same spectrum was recorded. The spectrum was a triplet with an hfs coupling constant of about 0.7 mT, and there was an indication of a further triplet splitting of about 0.2 mT.

Attempts to record the EPR spectrum of $1^{\bullet+}$ in fluid solution failed under conditions judged to be the most favourable ones for obtaining radical cation EPR spectra [oxidation by Tl$^{\rm III}$ trifluoroacetate in HFP,[10a] by phenyliodine(III) bis(trifluoroacetate) in HFP[13] or photolysis with DDQ in TFA at −12 °C or TFA–HFP at 0 °C[14]]. Only broad singlets with ΔH_{pp} ~ 0.42 mT and with indication of a further splitting of ~ 0.1 mT were seen, as exemplified in Fig. 4.

On the other hand, a weak spectrum could be recorded at high modulation amplitude upon thermal oxidation of dibenzofuran with *less reactive* reagents, such as 4-tolylthallium(III) trifluoroacetate in HFP or DDQ in HFP–trifluoroacetic acid. A spectrum obtained by the former method is shown in Fig. 5(*a*); it had a half-life of ≈20 min at room temperature. In principle, this spectrum might qualify as originating from $1^{\bullet+}$, and it was therefore necessary to trace its possible mode of formation.

Since 4-tolylthallium(III) trifluoroacetate was previously[10a]

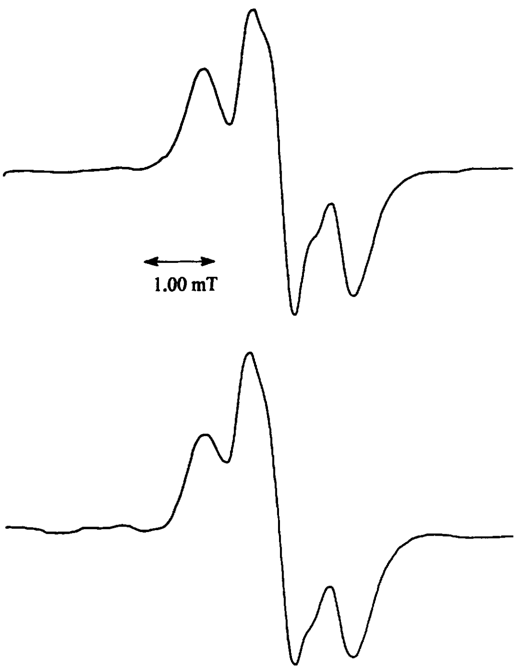


Fig. 3 EPR spectrum of dibenzofuran (upper trace) and 2-[^{2}H]dibenzofuran (lower trace) radical cation, obtained in a Freon matrix at −196 °C

Fig. 4 EPR spectrum, obtained by UV irradiation of a solution of dibenzofuran (10 mmol dm^{-3}) and thallium(III) trifluoroacetate (≈20 mmol dm^{-3}) in HFP at 22 °C

shown not to yield primary radical cations from substrates with $E°(ArH^{\bullet+}/ArH) \leqslant 1.6$ V (Ag/AgCl), the oxidation of dibenzofuran **1** with $E_{pa} \approx 1.9$ V by this reagent to give $1^{\bullet+}$ was deemed rather unlikely, especially since none of the more redox reactive dimethyldibenzofurans **2**–**5** and tetramethyldibenzofurans **6**, **7** in Table 1 gave any EPR spectrum upon oxidation by 4-tolylthallium(III) trifluoroacetate. Only the hexamethyl and octamethyl compounds (**8** and **9**) gave EPR spectra with this oxidant, thus confirming the upper limit of ArH redox activity, ≈1.6 V, found before.[10a] Instead, the quality of the dibenzofuran used (labelled '99+') was examined. The sample was pure according to TLC in two solvent systems, but GLC-MS analysis revealed the presence of two components (<0.1% of each) with slightly longer retention time than dibenzofuran. These were identified as fluorene and anthracene, respectively, and eventually it was shown that anthracene was responsible for the unknown EPR spectrum. This was obvious when the authentic (anthracene)$^{\bullet+}$ spectrum was recorded at the same fairly high modulation amplitude [Fig. 5(*b*)].

Compounds **2**, **5** and **6**, which according to cyclic voltammetry corresponded to unstable radical cations, also failed to give resolved spectra under the most favourable conditions tried, oxidation by thallium(III) trifluoroacetate in HFP at 22 °C or by DDQ (thermal or photochemical) in trifluoroacetic acid at −12 °C. By the same criterion, 2,8-dimethyldibenzofuran **3** should behave similarly, but here the Tl$^{\rm III}$–HFP method gave a resolved spectrum of a persistent radical cation superimposed on a broad singlet of $\Delta H_{pp} \approx 0.4$ mT [Fig. 6(*a*)]. The high-frequency component could be extracted by a forward-back Fourier transformation [Fig. 6(*b*)] and had a = 0.326 (6 H), 0.219 (2 H), 0.030 (2 H) and 0.011

Table 1 Electrochemical data for dibenzofuran, methyldibenzofurans and bidibenzofurans. Supporting electrolyte, Bu_4NPF_6 (0.15 mol dm^{-3})

Substituents (compound no.)	Sweep rate in DCM/V cm^{-1}	E_{rev} in DCM/V *vs.* Ag/AgCl[a]	Sweep rate in HFP/V cm^{-1}	E_{rev} in HFP/V *vs.* Ag/AgCl[b]
None (**1**)	0.2	1.9 (E_{pa})	40	1.51
1,9-Me_2 (**2**)	0.2	1.83 (E_{pa})	5	1.32
2,8-Me_2 (**3**)	0.2	1.75 (E_{pa})	20	1.31
3,7-Me_2 (**4**)	5	1.61		
4,6-Me_2 (**5**)	0.2	1.66 (E_{pa})	10	1.34
2,4,6,8-Me_4 (**6**)	0.2	1.83 (E_{pa})	5	1.19
1,3,7,9-Me_4 (**7**)	0.2	1.53		
1,3,4,6,7,9-Me_6 (**8**)	0.2	1.41		
Me_8 (**9**)	0.2	1.29		
2,2′-Bidibenzofuran (**10**)	0.1	1.54	0.1	1.11
3,3′-Bidibenzofuran (**11**)	0.1	1.54	0.1	1.17[c]
4,4′-Bidibenzofuran (**12**)			0.1	1.37 (E_{pa})
2,3′-Bidibenzofuran (**13**)	0.1	1.56	0.1	1.15[d]

[a] E_{rev} of ferricinium–ferrocene under these conditions = 0.43 V *vs.* Ag/AgCl. [b] E_{rev} of ferricinium–ferrocene under these conditions = 0.05 V *vs.* Ag/AgCl. [c] In HFP–dichloromethane (1 : 1 v : v). [d] In HFP–dichloromethane (3 : 1 v : v).

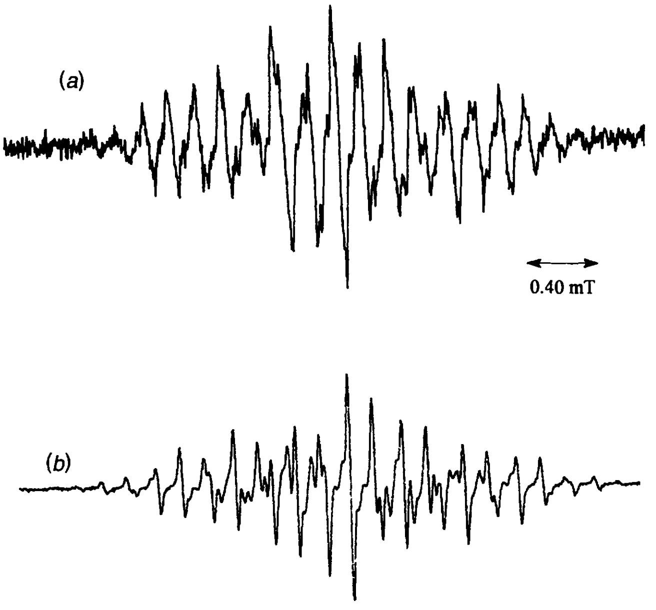


Fig. 5 EPR spectrum, obtained by (*a*) reaction of dibenzofuran (99+%, 20 mmol dm^{-3}) and 4-tolylthallium(III) trifluoroacetate (≈20 mmol dm^{-3}) in HFP at 22 °C at a microwave power of 1.25 mW and modulation amplitude of 0.08 mT, and (*b*) of anthracene (saturated solution) under the same conditions

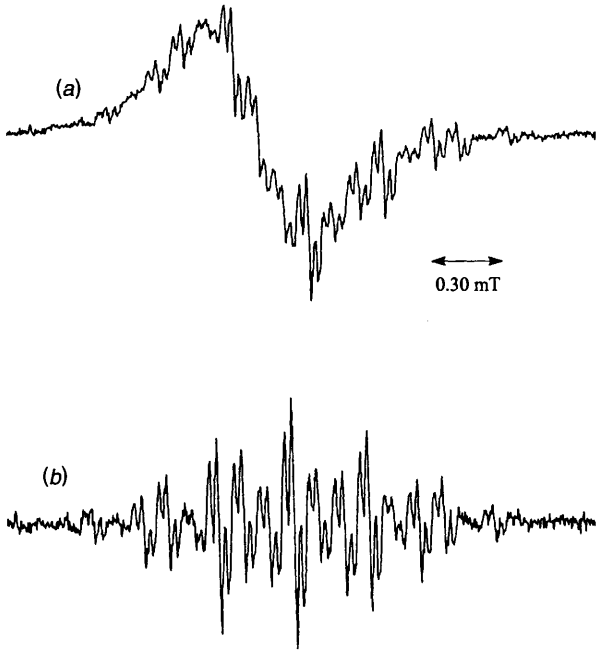


Fig. 6 EPR spectrum, obtained by (*a*) reaction of 2,8-dimethyldibenzofuran (**3**, saturated solution) and thallium(III) trifluoroacetate (≈20 mmol dm^{-3}) in HFP at 22 °C and (*b*) removal of the low-frequency component of this spectrum by a forward-back Fourier transformation

(2 H) mT. The generation and quality of this spectrum was dependent on the mixing conditions; sometimes it appeared only weakly on top of a strong singlet, and sometimes it appeared almost unperturbed by the singlet. When 4-tolylthallium(III) trifluoroacetate was used as the oxidant, a weak spectrum of the same appearance as in Fig. 6(*b*) was obtained.

Compounds **7**–**9** gave resolved spectra of highly persistent radical cations, and the coupling constants were determined from the spectra (see Table 2). The assignments are based on the reasoning given in the Discussion part.

The 2,2′-dehydrodimer **10** upon treatment with thallium(III) trifluoroacetate in HFP gave a persistent EPR spectrum (Fig. 7); similar, but weaker spectra were seen in TFA–DDQ–*hν* at − 12 °C. The following hfs constants could be extracted from the HFP spectrum: 0.245 (2 H), 0.171 (2 H), 0.083 (2 H), 0.060 (2 H), 0.040 (2 H) and 0.018 (2 H) mT. Under conditions of low resolution, the spectrum degenerated into a quintet of broad peaks, with splittings of 0.17–0.24 mT.

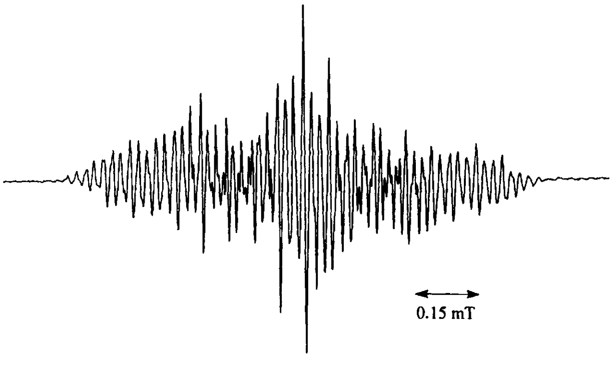


Fig. 7 EPR spectrum obtained by oxidation of a saturated solution of **10** by thallium(III) trifluoroacetate in HFP at 22 °C

The 3,3′-dehydrodimer **11** under the same conditions as **10** gave a resolved spectrum (Fig. 8) which persisted for 3–4 h. The 4,4′-dehydrodimer **12** gave only a broad (ΔH_{pp} about 0.2 mT) unresolved singlet upon oxidation by Tl^{III} trifluoroacetate in HFP. In HFP–TFA (5:2 v/v) fine black particles precipitated, and a strong signal with ΔH_{pp} = 0.031 mT was recorded.

2,3′-Bidibenzofuran **13** upon oxidation by Tl^{III} trifluoroacetate in HFP gave a resolved spectrum [Fig. 9(*a*)] which lost most of its resolution within 1–2 h [Fig. 9(*b*)]. The final spectrum had some resemblance to the spectrum obtained from

Table 2 EPR spectral data for radical cations of dibenzofuran, methyldibenzofurans and bidibenzofurans

		hfs constants/mT (multiplicity)			
Substituents (compound no.)	Method[a]	$a_{1,9}$	$a_{2,8}$	$a_{3,7}$	$a_{4,6}$
None (**1**)	A	*b*			
	B	*c*			
	C			0.7 (2)	
1,9-Me_2 (**2**)	A	*d*			
	B	*d*			
2,8-Me_2 (**3**)	A		See text		
	B	*e*			
3,7-Me_2 (**4**)	A	0.212 (2)	0.056 (2)	0.900 (6)	0.056 (2)
	B	0.214	0.056	0.906	0.056
4,6-Me_2 (**5**)	A	*d*			
	B	*d*			
2,4,6,8-Me_4 (**6**)	A	*d*			
	B	*d*			
1,3,7,9-Me_4 (**7**)	A	0.287 (6)	0.029 (2)	0.810 (6)	0.013 (2)
	B	0.279	0.027	0.837	0.013
1,3,4,6,7,9-Me_6 (**8**)	A	0.336 (6)	<0.002	0.806 (6)	0.0085 (6)
	B	0.336	0.004	0.813	0.004
Me_8 (**9**)	A	0.271 (6)	0.008 (6)	0.731 (6)	0.092 (6)
	B	0.275	0.008	0.751	0.082
2,2′-, 3,3′-, 4,4′- and 2,3′-bidibenzofuran (**10**–**13**)	A		See text		

[a] A = oxidation by Tl^{III} trifluoroacetate in HFP at 22 °C; B = thermal or photochemical oxidation by DDQ in trifluoroacetic acid at −12 °C; C = oxidation by γ rays in a $CFCl_3$ matrix at −196 °C. [b] No signal seen. [c] Broad singlet after irradiation for 20 min by UV light. [d] Broad singlet. [e] Spectrum too weak.

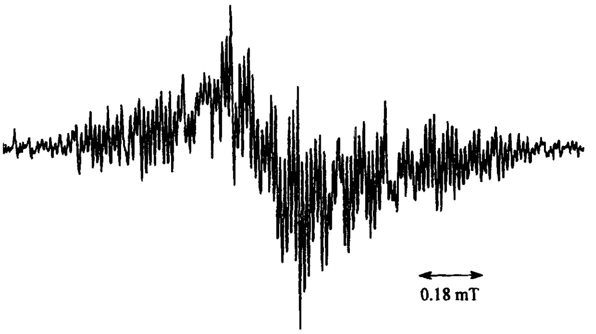


Fig. 8 EPR spectrum obtained by oxidation of a saturated solution of **11** by thallium(III) trifluoroacetate in HFP at 22 °C

dibenzofuran itself (Fig. 4). Attempts at simulating this spectrum showed that it must be composed of primarily doublets, indicating that most of the spin density is centered in one of the dibenzofuran moieties.

Discussion

The low-temperature EPR spectrum of $1^{\bullet +}$ showed the presence of a triplet with an hfs coupling constant of 0.7 mT (Fig. 3). The experiment with 2-[^{2}H]dibenzofuran showed that this coupling cannot be to the 2,8-hydrogens, since the spectrum was unchanged. Most likely, this is the coupling constant to the 3,7-hydrogens.

No fluid solution EPR spectrum of $1^{\bullet +}$ could be obtained. The spectrum obtained by 4-tolylthallium(III) trifluoroacetate oxidation of **1** of high commercial quality [Fig. 5(*a*)] was shown to originate from anthracene, present in the commercial sample as an impurity at the 0.1% level. The spectra obtained from $1^{\bullet +}$ under more vigorous oxidizing conditions (example, see Fig. 4) are badly resolved and probably originate from radical cations of various oligodehydrodimers. This is also suggested by the facile anodic polymerization of **1** (Fig. 2) which was earlier found by Rault-Berthelot and Simonet.[11] It is likely that the transformation of the EPR spectrum of the 4,4′- and 2,3′-dehydrodimer radical cations ($12^{\bullet +}$ and $13^{\bullet +}$) into a spectrum resembling that obtained from the oxidation of dibenzofuran [compare Figs. 4 and 9(*b*)] reflects an oligomerization process (see below).

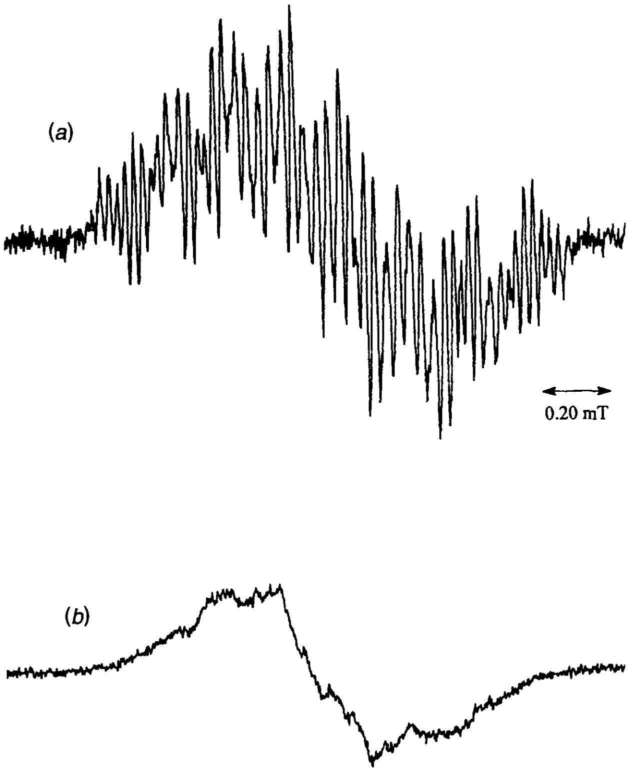
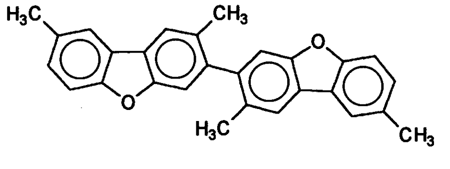


Fig. 9 EPR spectrum obtained by oxidation of a saturated solution of **13** by thallium(III) trifluoroacetate in HFP at 22 °C after (*a*) 10 min and (*b*) 2 h

Thus the assignment of the hfs coupling constants of $1^{\bullet +}$ must rest on indirect evidence. The large coupling constant of 0.90 mT in the spectrum of the 3,7-dimethyl substituted $4^{\bullet +}$ must be assigned to the methyl groups in the 3,7-positions because of its multiplicity, and the second largest one (0.212 mT) to the 1,9-positions in analogy with the assigment of the second largest coupling constant (0.287 mT) in the spectrum of $7^{\bullet +}$ to the methyl groups in the 1,9-positions, again from its multiplicity. The spectrum of the hexamethyl derivative $8^{\bullet +}$

Table 3 Theoretical and experimental spin density distributions in **1**$^{\bullet +}$, compared to isomer distributions from various reactions between **1**$^{\bullet +}$ and radicals or nucleophiles

Reaction of 1$^{\bullet +}$ with	Isomer distribution (%) 1-	2-	3-	4-	Ref.
CN^- in MeOH (anodic)	8	17	71	4	6
CN^- in MeOH (*hν*)	9	27	64	< 0.5	6
AcO^- in HOAc (anodic)	32	3	62	3	5
AcO^- in HOAc [12-tungstocobaltate(III)]	42	1	55	2	5
AcO^- in HOAc [$Ce^{IV}(NO_3)_6{}^{2-}$]	32	2	64	2	5
AcO^- in HOAc (Ag^{II}–$S_2O_8{}^{2-}$)	29	1	70		5
$(NO_2)_3C^-$ in CH_2Cl_2 [*hν* with $C(NO_2)_4$]	62		38		3*b*
$(NO_2)_3C^-$ in CH_3CN [*hν* with $C(NO_2)_4$]	51		49		3*b*
NO_2 in CH_2Cl_2 (HNO_2 catalysed nitration)	10	12	78	< 0.1	3
NO_2 in HFP [*hν* with $C(NO_2)_4$]	6	9	71	14	3*b*
Theoretical spin density distribution of the $^2A_2$ state of **1**$^{\bullet +}$, normalized over positions 1–4	18	6	59	16	3*a*, 15
Theoretical spin density distribution of the $^2B_1$ state of **1**$^{\bullet +}$, normalized over positions 1–4	12	37	17	32	3*a*, 15
Experimental spin density distribution in **1**$^{\bullet +}$, normalized over positions 1–4	25	1	67	7	This work



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then serves to establish that the hfs coupling constant to the 4,6-positions in all likelihood is the third largest one and that the smallest one must be to the 2,8-positions. The assignments to the positions of the octamethyl species **9**$^{\bullet +}$ follow from the reasoning above.

From their cyclic voltammetric behaviour, compounds **2**, **3**, **5** and **6** should correspond to reactive radical cations, and indeed no EPR spectra attributable to the primary radical cations could be recorded. Only broad singlet spectra, presumably originating from dehydrooligomer radical cations, were obtained. However, oxidation of **3** by thallium(III) trifluoroacetate in HFP produced a well resolved spectrum of a persistent radical cation (Fig. 5) superimposed upon the broad singlet, to which we assign the structure of a 3,3′-connected dehydrodimer **14**. Dehydrodimer formation from radical cations is a well documented reaction,[9] and since the spectrum of Fig. 5 lacks a large coupling constant to a hydrogen in the 3-position, it is reasonable to assume that dehydrodimer **14** is responsible for the spectrum.

Returning to the assignments of hfs coupling constants to the various positions in **1**$^{\bullet +}$, these are likely to be reflected in those of the octamethyldibenzofuran radical cation (**9**$^{\bullet +}$), since in the latter each carbon atom has been perturbed by a methyl group in an approximately equal manner, apart from some possibly modifying effect due to the methyl–methyl interaction between the 1- and 9-positions. Qualitatively, these assignments are in agreement with the calculated spin densities in **1**$^{\bullet +}$ [Fig. 1(*a*)]. The preponderance of attack at the 3-position of **1**$^{\bullet +}$ by radicals or nucleophiles (for examples, see Table 3) thus is in agreement with the experimentally determined spin density distribution of the $^2A_2$ state of the radical cation [Fig. 1(*b*); note that the two lowest radical cation states are nearly degenerate and that only the spin density distribution of the $^2A_2$ state correctly predicts the results of the **1**$^{\bullet +}$-radical reaction], or the combined distribution of LUMO coefficients of the $^2B_1$ [Fig. 1(*a*)] or $^2A_2$ states (in this case the distribution of LUMO coefficients is nearly the same in the two states) and spin densities in the $^3B_2$ triplet state.[15]

The behaviour of the radical cations of the dehydrodimers is of some interest. Both **10** and **11** show reversible electrochemical behaviour upon CV at 0.1 V s^{-1} and dichloromethane and HFP and both give fairly persistent EPR spectra of the corresponding radical cations upon oxidation in HFP. It is probable that the spin density is largely localized in the two connected rings, and thus **10**$^{\bullet +}$, being formally a 4,4′-bisoxygen substituted biphenyl, will be a relatively stable species. In **11**$^{\bullet +}$, both the reactive 3,3′-positions are blocked. On the other hand, the 4,4′-connected dimer radical cation **12**$^{\bullet +}$ will have the reactive 3,3′-positions available for coupling. In the unsymmetrical **13**$^{\bullet +}$, the spin density resides largely in one of the dibenzofuranyl moieties and thus will confer a higher reactivity to that part of the radical cation.

Theoretical calculations on the electronic properties of poly(3,3′-dibenzofuran) by semiempirical methods were reported some years ago by Burke *et al.*[16] The structure of the polymer was approximated by that of monomeric **1**, except for the 3,3′-connecting carbon–carbon bond which was taken from the corresponding dimer **11** structure. One predicted experimental parameter was E_O, the oxidation potential of the polymer, which came out at 0.9 V (SCE). The value measured in HFP (Fig. 2) was 1.0 V (Ag/AgCl) which after calibration against the ferricinium/ferrocene potential (0.05 V *vs.* Ag/AgCl in HFP) translates into a value of 1.4 V (SCE), in reasonable agreement with the calculated value, considering the approximations involved. A second experimental value 'between 0.5 and 1.0 V' [*vs.* Ag–Ag^+ (0.1 mol dm^{-3})] for the reversible potential of the polymer film was obtained[11] in acetonitrile–Bu_4NPF_6; this corresponds to a value between 0.9 and 1.4 V *vs.* SCE.

The finding that the electropolymerization of dibenzofuran could be performed in HFP prompted us to study a few other systems (see Experimental section) in order to briefly elucidate the properties of HFP for the study of conducting polymers.[17] As expected, the stabilizing effect of HFP upon radical cations led to a decreased tendency for polymerization to occur, presumably due to slower kinetics. A disadvantage with HFP is the rather low solubility of high molecular weight or non-polar aromatic compounds, in some cases making studies above a concentration level of 0.5 mmol dm^{-3} not feasible.

Experimental

Materials and methods

Dibenzofuran **1** was of Aldrich 99 + % quality and was purified by a chemical method involving Cu reduction of 3-iododibenzofuran which removed the anthracene impurity (see below). The synthesis of 2-[^{2}H]dibenzofuran was performed according to a literature method.[18] The synthesis and purification of compounds **2**–**9** was described earlier.[8] HFP, dichloromethane and trifluoroacetic acid were of Merck UVASOL quality.

EPR spectra in fluid solution were recorded by the Upgrade Version ESP 3220–200SH of a Bruker ER-200D spectrometer.

Photolyses were performed in the photolysis cavity (ER 4104 OR), using a 50 W high-pressure Hg lamp from Bruker (ER 202). The EPR spectra were recorded as described[10a] (100 kHz modulation frequency, microwave power 0.4–1.6 mW, modulation amplitude 0.001–0.04 mT). The matrix experiments at -196 °C were performed on solutions (0.1–1.0% by wt.) of dibenzofuran or 2-[^{2}H]dibenzofuran in $CFCl_3$ (BDH). These were frozen in liquid nitrogen in Suprasil tubes prior to exposure to X-rays from a ^{60}Co source to a nominal dose of 1 Mrad. EPR spectra at -196 °C were recorded using a Varian E9 spectrometer.

Cyclic voltammetry was performed by a BAS-100 instrument in dichloromethane- or HFP-Bu_4NPF_6 (0.15 mol dm^{-3}) at a Pt button electrode. The reference electrode was an Ag/AgCl electrode. In HFP, the ferricinium/ferrocene couple had $(E_{pa} + E_{pc})/2 = 0.05$ V *vs.* Ag/AgCl.

2,2′-Bidibenzofuran 10. This was obtained from Ullman coupling of 2-iododibenzofuran.[19] δ_H(300 MHz; $CDCl_3$): 8.23 (dd, 1.9, 0.3 Hz, 2 H), 8.04 (ddd, 7.6, 1.4, 0.5 Hz, 2 H), 7.77 (dd, 8.5, 1.9 Hz, 2 H), 7.67 (dd, 8.5, 0.3 Hz, 2 H), 7.62 (ddd, 8.3, 1.1, 0.5 Hz, 2 H), 7.50 (ddd, 8.3, 7.3, 1.4 Hz, 2 H), 7.39 (ddd, 7.6, 7.3, 1.1 Hz, 2 H); mp 228–230 °C, lit.,[19] 227–230 °C; *m/z* for M^+ 334 (100%).

3,3′-Bidibenzofuran 11. This was prepared from 3-iododibenzofuran and palladium(II) acetate, a method originally used to make biphenyls.[20] δ_H(300 MHz; $CDCl_3$): 8.05 (d, 8.1 Hz, 2 H), 8.00 (ddd, 7.6, 1.4, 0.7 Hz, 2 H), 7.89 (d, 1.5 Hz, 2 H), 7.70 (dd, 8.1, 1.5 Hz, 2 H), 7.62 (ddd, 8.2, 1.0, 0.7 Hz, 2 H), 7.49 (ddd, 8.2, 7.4, 1.4 Hz, 2 H), 7.38 (ddd, 7.6, 7.4, 1.0 Hz, 2 H); mp 249–251 °C, lit.,[21] 252.5 °C; *m/z* for M^+ 334 (100%).

An attempt to make this compound with an Ullman coupling resulted in the formation of dibenzofuran, possessing the advantage of being free from anthracene, and a low yield of *2,3′-bidibenzofuran* 13. δ_H(300 MHz; $CDCl_3$): 8.24 (dd, 1.9, 0.3 Hz, 1 H), 8.03 (broad d, 8.0 Hz, 2 H), 7.99 (ddd, 7.6, 1.4, 0.7 Hz, 1 H), 7.86 (d, 1.6 Hz, 1 H), 7.78 (dd, 8.6, 1.9 Hz, 1 H), 7.68 (dd, 8.0, 1.6 Hz, 1 H), 7.67 (dd, 8.6, 0.3 Hz, 1 H), 7.61 (broad d, 8.0 Hz, 2 H), 7.50 (ddd, 8.0, 7.3, 1.4 Hz, 1 H), 7.49 (ddd, 8.0, 7.4, 1.4 Hz, 1 H), 7.39 (ddd, 7.6, 7.3, 1.0 Hz, 1 H), 7.38 (ddd, 7.6, 7.4, 1.0 Hz, 1 H); mp 133–135 °C; *m/z* 334 for M^+ (100%).

4,4′-Bidibenzofuran 12. This was obtained from the iron(III) acetylacetonate-mediated coupling of monolithiated dibenzofuran.[22] δ_H(300 MHz; $CDCl_3$): 8.06 (dd, 7.7, 1.3 Hz, 2 H), 8.05 (ddd, 7.6, 1.4, 0.7 Hz, 2 H), 8.00 (dd, 7.6, 1.3 Hz, 2 H), 7.58 (ddd, 7.1, 1.1, 0.7 Hz, 2 H), 7.55 (dd, 7.7, 7.6 Hz, 2 H), 7.48 (ddd, 7.9, 7.6, 1.4 Hz, 2 H), 7.39 (ddd, 7.9, 7.1, 1.1 Hz, 2 H); mp 192–195 °C, lit.,[23] 191 °C; *m/z* 334 for M^+ (100%).

Tests of HFP–Bu_4NPF_6 as a medium for electropolymerization. Azulene ($E_{pa} = 0.65$ V) showed no sign of polymerization at a concentration of <1 mmol dm^{-3}. Dibenzothiophene exhibited reversibility at $v = 20$ V s^{-1}, $(E_{pa} + E_{pc})/2 = 1.26$ V *vs.* Ag/AgCl, and no buildup of polymer was seen at $v = 0.1$ V s^{-1} at [dibenzothiophene] = 9 mmol dm^{-3}. *N*-Phenylcarbazole at a concentration of 5 mmol dm^{-3} did not give any polymer, but a new, reversible redox couple with $(E_{pa} + E_{pc})/2 = 0.75$ V *vs.* Ag/AgCl developed. At a concentration of 15 mmol dm^{-3}, polymer formation was observed from *N*-phenylcarbazole. Dibenzofuran, see text above.

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