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Anodic oxidation of aminated dibenzothiophenes: isolation of stable radical cation salts of 3,7-diaminodibenzothiophene and 3,7-bis(dimethylamino)dibenzothiophene

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Summary — Several dibenzothiophenes substituted with aminated electron-donating groups (amino or dimethylamino) were synthesized with the objective of converting them into stable cation radical salts by anodic oxidation. The first step of their preparation was always a nitration: of dibenzothiophene, for the products substituted in the 2-position or in the 2- and 8-positions; of dibenzothiophene oxide, for the products substituted in the 3-position or in the 3- and 7-positions; and of 2,8-dibromodibenzothiophene, for the products substituted in the 2-, 3-, 7- and 8-positions. In cyclic voltammetry, most of these aminated dibenzothiophenes exhibited a reversible first oxidation peak, at least, but only 3,7-diaminodibenzothiophene and 3,7-bis(dimethylamino)dibenzothiophene led to stable cation radical salts, isolated as, respectively, black and blue-green crystals characterized by ESR spectroscopy.

diaminodibenzothiophene / bis(dimethylamino)dibenzothiophene / anodic oxidation / cation radical salt

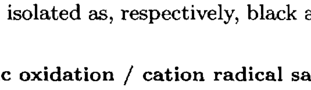
Résumé — Oxydation anodique de dibenzothiophènes aminés: isolement de sels de radicaux cations stables du 3,7-diaminodibenzothiophène et du 3,7-bis(diméthylamino)dibenzothiophène. *Plusieurs dibenzothiophènes substitués par des groupements électrodonneurs aminés (amino ou diméthylamino) ont été synthétisés dans le but de les transformer, par oxydation anodique, en sels de radicaux cations stables. La première étape de leur préparation est toujours une nitration : du dibenzothiophène pour les produits substitués en position 2 ou en positions 2 et 8 ; de l'oxyde de dibenzothiophène, pour les produits substitués en position 3 ou en positions 3 et 7 ; et du 2,8-dibromodibenzothiophène, pour les produits substitués en positions 2, 3, 7 et 8. En voltampérométrie cyclique, la majorité de ces dibenzothiophènes aminés présentent au moins un premier pic d'oxydation réversible, mais seuls le 3,7-diaminodibenzothiophène et le 3,7-bis(diméthylamino)dibenzothiophène conduisent à des sels de radicaux cations stables, isolés sous forme de cristaux respectivement noirs et bleu-vert caractérisés par spectroscopie de RPE.*

diaminodibenzothiophène / bis(diméthylamino)dibenzothiophène / oxydation anodique / sel de radical cation

Introduction

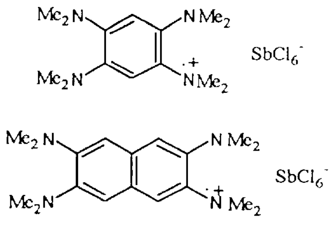
Previously we obtained deep blue crystals of stable cation radical salts of 2,3,7,8-tetramethoxydibenzothiophene and 2,3:7,8-bis(methylenedioxy)dibenzothiophene [1]. These results prompted us to study the behavior in anodic oxidation of dibenzothiophenes substituted by other electron-donating groups such as amino and dimethylamino in the hope of converting them, as well, into stable cation radical salts.

Aromatic hydrocarbons (eg, benzene, naphthalene and biphenyl) substituted with amino and dialkylamino groups were the subject of electrooxidation studies. The first example of this kind of stable cation radical salt is the 1,4-bis(dimethylamino)benzene cation radical perchlorate, known ever since 1879 under the name of Wurster's blue [2] (scheme 1).



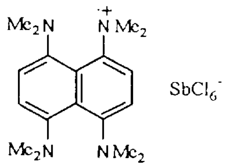
Scheme 1

Elbl-Weiser et al [3] prepared, by chemical oxidation with tris(4-bromophenyl)aminium hexachloroantimonate, isolable and stable cation radical salts of 1,2,4,5-tetrakis(dimethylamino)benzene and 2,3,6,7-tetrakis(dimethylamino) naphthalene (scheme 2).



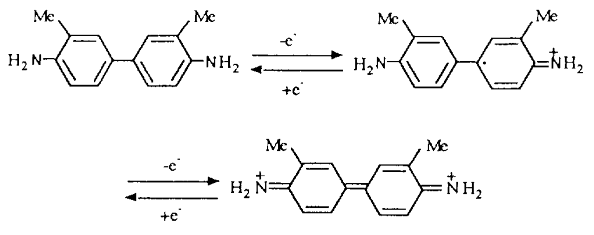
Scheme 2

Likewise Barth et al [4] showed that the same tris(4-bromophenyl)aminium hexachloroantimonate (or iodine) allows generation of the cation radical of 1,4,5,8-tetrakis(dimethylamino)naphthalene (scheme 3).



Scheme 3

Blount et al [5] electrogenerated readily, in CH_2Cl_2/Et_4NClO_4, the isolable and stable cation radical of 3,3′-dimethyl-4,4′-diaminobiphenyl, but in $MeCN/Et_4NClO_4$ the cation radical salt was soluble and the electrolysis proceeded until the formation of the diiminium salt (scheme 4).



Scheme 4

Dvorak et al [6] ascertained that the electrooxidation of *N*,*N*,*N*′,*N*′-tetramethylbenzidine, in acetonitrile, proceeds via a fairly stable intermediate cation radical to lead to a diiminium salt (scheme 5).

Saget et al [7] reported that the electrogenerated cation radical of *N*,*N*,*N*′,*N*′-tetramethylbenzidine, in $MeCN/LiClO_4$, seemed to be stable but was not isolated. Lastly Delahaye et al [8] pointed out that the electrooxidation of this tetramethylbenzidine, in $MeNO_2/Me_4NClO_4$, gave an isolable but poorly stable blue-green solid.

Synthesis

To study the influence of the position and number of the electron-donating groups amino and dimethylamino, upon the electrooxidation of dibenzothiophenes, several target molecules were synthesized.

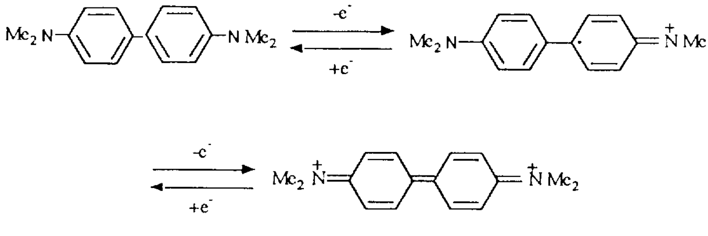
Whatever the position(s) to be substituted, the first step is always a nitration of dibenzothiophene (for the compounds substituted in the 2-position or in the 2- and 8-positions), of dibenzothiophene oxide (for the compounds substituted in the 3-position or in the 3- and 7-positions) and of 2,8-dibromodibenzothiophene (for the compounds substituted in the 2-, 3-, 7- and 8-positions).

Compounds monosubstituted in the 2-position: 2-aminodibenzothiophene **1a** *and 2-(dimethylamino)-dibenzothiophene* **1b**

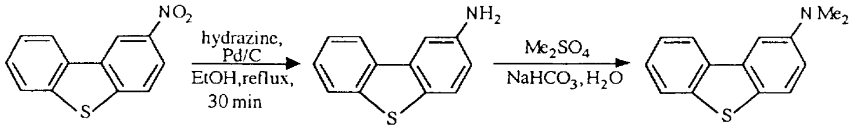
2-Nitrodibenzothiophene prepared by direct nitration [9] led, after reduction by hydrazine, to 2-aminodibenzothiophene **1a** [10] which, by reaction with dimethyl sulfate, gave a new compound 2-(dimethylamino)dibenzothiophene **1b** (scheme 6).

Compounds disubstituted in the 2- and 8-positions: 2,8-diaminodibenzothiophene **2a** *and 2,8-bis(dimethylamino)dibenzothiophene* **2b**

As a preliminary step 2,8-dinitrodibenzothiophene has to be prepared by nitration of 2-nitrodibenzothiophene

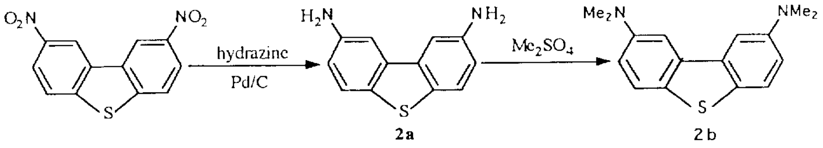


Scheme 5

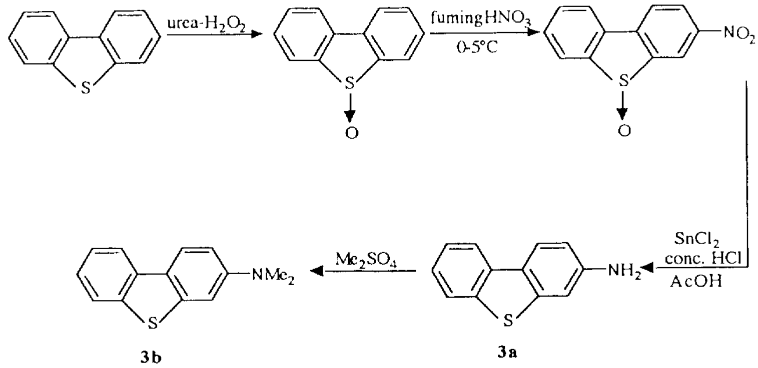


1a **1b**

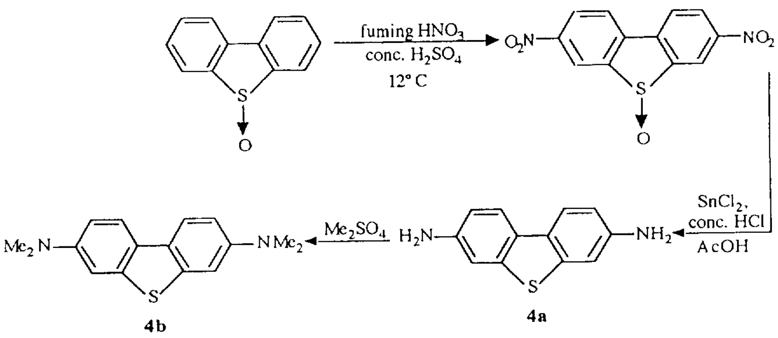
Scheme 6



Scheme 7



Scheme 8



Scheme 9

[11]. The reduction of this dinitro derivative with hydrazine led to 2,8-diaminodibenzothiophene **2a**, methylation of which, as above, gave a new compound 2,8-bis(dimethylamino)dibenzothiophene **2b** (scheme 7).

Compounds monosubstituted in the 3-position: 3-aminodibenzothiophene **3a** *and 3-(dimethylamino)dibenzothiophene* **3b**

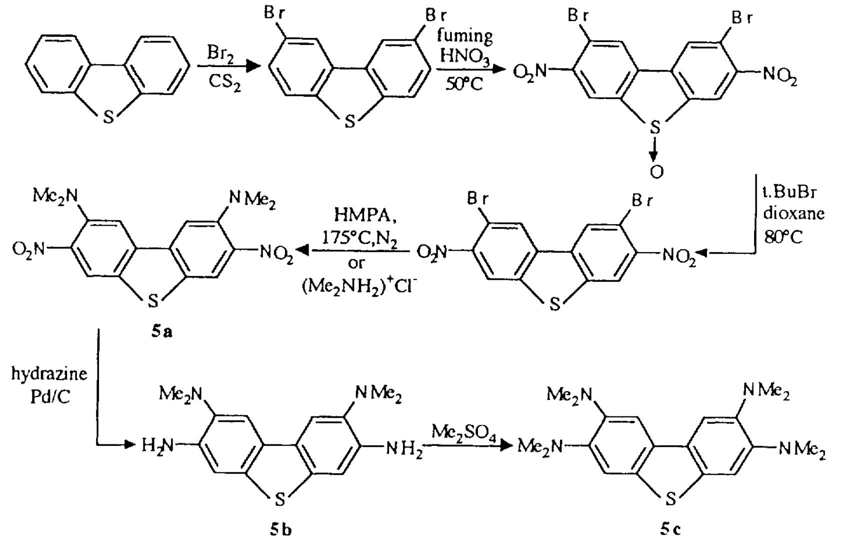
For this purpose, one must start from dibenzothiophene sulfoxide [12] in order to orientate the nitration in the 3-position [13]. The reduction of the nitro derivative thus obtained with a solution of stannous chloride in concentrated hydrochloric acid led to 3-aminodibenzothiophene **3a** [13], methylation of which gave 3-(dimethylamino)dibenzothiophene **3b** (scheme 8).

Compounds disubstituted in the 3- and 7-positions: 3,7-diaminodibenzothiophene **4a** *and 3,7-bis-(dimethylamino)dibenzothiophene* **4b**

The dinitro derivative obtained by dinitration in the 3- and 7-positions of dibenzothiophene oxide was reduced, as above, by stannous chloride into 3,7-diaminodibenzothiophene **4a** [14], methylation of which led to 3,7-bis(dimethylamino)dibenzothiophene **4b** (scheme 9).

Compounds tetrasubstituted in the 2-, 3-, 7- and 8-positions: 2,8-bis(dimethylamino)-3,7-dinitrodibenzothiophene **5a**, *2,8-bis(dimethylamino)-3,7-diaminodibenzothiophene* **5b** *and 2,3,7,8-tetrakis(dimethylamino)dibenzothiophene* **5c**

The first step was the dibromination of dibenzothiophene in the 2- and 8-positions [15], followed by the preparation of 2,8-dibromo-3,7-dinitrodibenzothiophene 5-oxide by reaction with fuming nitric acid at 50 °C [16]. The reduction of this sulfoxide into a sulfide was carried out by reaction with *tert*-butyl bromide in dioxane. The reaction of 2,8-dibromo-3,7-dinitrodibenzothiophene with hexamethylphosphoramide(HMPA) or dimethylammonium chloride led to 2,8-bis(dimethylamino)-3,7-dinitrodibenzothiophene **5a**, reduction of which with hydrazine gave 2,8-bis-(dimethylamino)-3,7-diaminodibenzothiophene **5b**.



Scheme 10

Table I. Oxidation peak potentials of amino and diaminodibenzothiophenes and their methylated derivatives ($c = 2.5 \times 10^{-3}$ M) at a platinum microanode in MeCN/LiClO$_4$ 0.1 M; sweep rate = 100 mVs^{-1}; reference = Ag/Ag$^+$ 0.01 M.

Ep (V)	**1a** *2-NH$_2$*	**1b** *2-NMe$_2$*	**2a** *2,8-NH$_2$*	**2b** *2,8-NMe$_2$*	**3a** *3-NH$_2$*	**3b** *3-NMe$_2$*	**4a** *3,7-NH$_2$*	**4b** *3,7-NMe$_2$*
First step	0.59	0.38 (rev)	0.48	0.23 (rev)	0.50	0.45 (rev)	0.18 (rev)	0.10 (rev)
Second step	1.35	1.04	1.36	0.52 (rev)	1.30	1.12	0.51 (rev)	0.38 (rev)
Third step	1.45	1.39			1.44	1.43		

Lastly the methylation of **5b** allowed us to isolate 2,3,7,8-tetrakis (dimethylamino)dibenzothiophene **5c** (scheme 10).

Since the anodic oxidation of certain methoxydibenzothiophenes [1] and amino or dimethylaminodibenzothiophenes (see the following) led to stable cation radical salts, we intended to add up the electron-donating effects of OMe and NR$_2$ groups in the same molecule of dibenzothiophene, by the preparation, for instance, of 2,8-dimethoxy-3,7-diaminodibenzothiophene and its tetramethylated derivative. But several attempts failed, from both commercial 3,3′-dimethoxybenzidine and 2,8-dimethoxydibenzothiophene [1].

Anodic behavior of aminated dibenzothiophenes

Cyclic voltammetry

Cyclic voltammetry measurements were carried out from solutions of aminated dibenzothiophenes 2.5×10^{-3} M in MeCN/LiClO$_4$ 0.1 M (unless otherwise stated), with a platinum microanode ($A = 0.785$ mm^2) as a working electrode and a silver electrode (a silver wire dipped into a 10^{-2} M solution of silver nitrate in acetonitrile) as a reference electrode.

Table I gathers oxidation peak potentials of dibenzothiophenes mono or disubstituted by NH$_2$ or NMe$_2$ groups. In the case of monosubstituted derivatives (**1a** and **3a** on the one hand; **1b** and **3b** on the other), the values of the potentials are very close together whatever the position of the substituent. However 3,7-disubstituted derivatives (**4a** and **4b**) are more readily oxidizable than their 2,8-disubstituted isomers (**2a** and **2b**); this can be explained by a better conjugation of the NH$_2$ or NMe$_2$ groups with the aromatic rings of the biphenyl moiety of dibenzothiophene when these groups are placed in the *para* position, namely in the 3,7-positions of dibenzothiophene, or by a better stability of the radical cation and dication.

Compounds **1a**, **2a** and **3a** do not show a reversible anodic peak; on the other hand, in the case of methoxylated derivatives **1b** and **3b**, the first oxidation peak is clearly reversible (see fig 1a and b); compounds **2b**, **4b** and **4a** exhibit two reversible oxidation peaks (see fig 1c, 1d and 2). In all the cases of reversibility, it was a one-electron process (Epa-Epc = 60 mV).

Let us also note that, in the case of compounds **1a**, **2a** and **3a**, a passivation phenomenon occurs after a few anodic sweeps, unlike compounds **1b**, **2b**, **3b** and **4b**. In the case of compound **4a**, in CH$_2$Cl$_2$/nBu$_4$NBF$_4$ 0.1 M at a concentration of 1.25×10^{-3} M, after several sweeps the oxidation peaks at 0.18 and 0.51 V disappear progressively, whereas a new peak appears simultaneously at 0.90 V (fig 2); this is probably due to deposition by electrocrystallization of the **4a** cation radical perchlorate onto the anode.

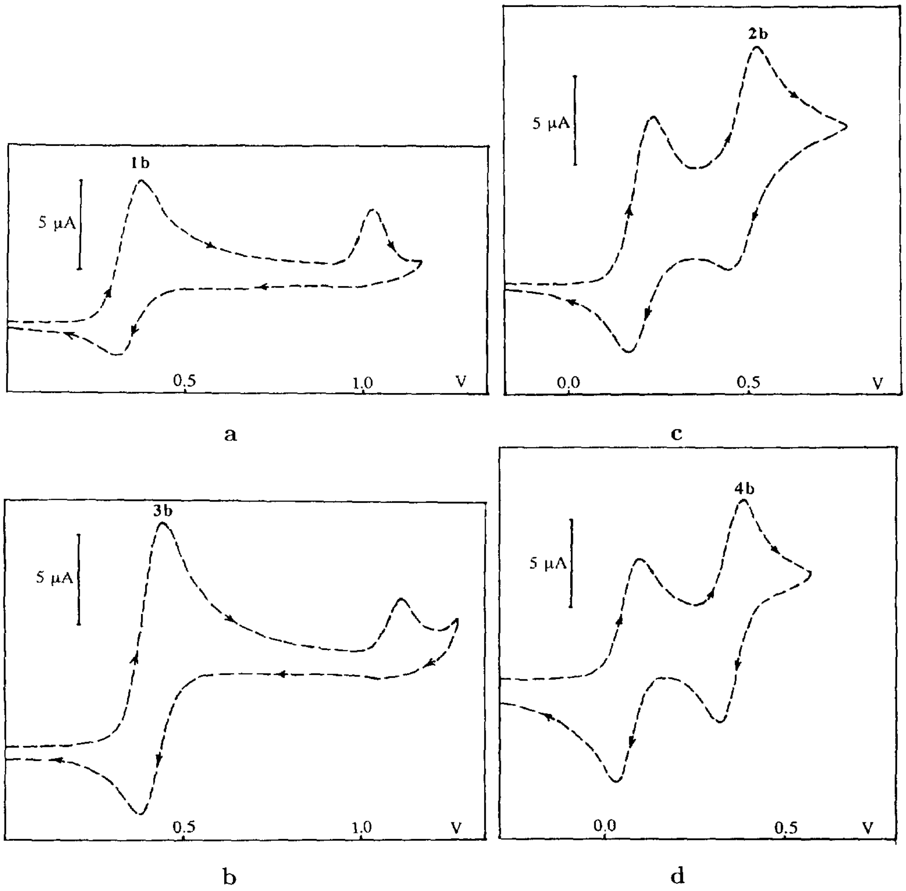


Fig 1. Cyclic voltammetry (v = 100 mVs^{-1}) of aminated dibenzothiophenes **1b**, **3b**, **2b** and **4b** (c = 2.5 mM in MeCN/LiClO$_4$ 0.1 M); Pt microanode; reference: Ag/Ag$^+$ 0.01 M in MeCN: a: 2-(dimethylamino)dibenzothiophene **1b**; b: 3-(dimethylamino)dibenzothiophene **3b**; c: 2,8-bis(dimethylamino)dibenzothiophene **2b**; d: 3,7-bis(dimethylamino)dibenzothiophene **4b**.

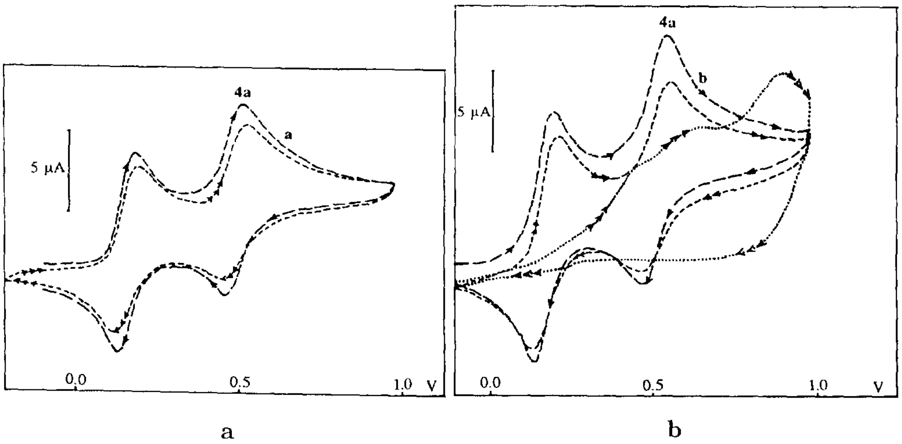
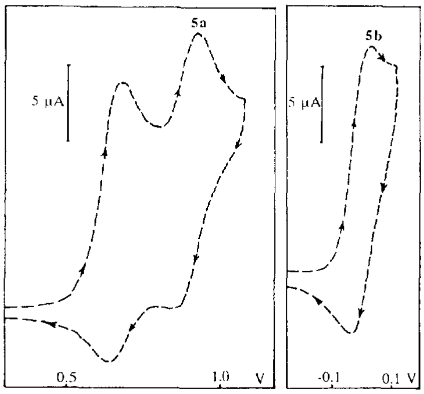


Fig 2. Cyclic voltammetry with repetitive sweeps (v = 100 mVs^{-1}) of 3,7-diaminodibenzothiophene **4a** [c = 1.25 mM, in: a) MeCN/LiClO$_4$ 0.1 M, b) CH$_2$Cl$_2$/nBu$_4$NClO$_4$ 0.1 M]; Pt microanode; reference: Ag/Ag$^+$ 0.01 M in MeCN.

Table II allows us to compare cyclic voltammetry data relative to the series of tetrasubstituted compounds **5a**, **5b** and **5c**. Compounds **5a** and **5c** exhibit two reversible oxidation steps (fig 3a and 4a) whereas in the case of compound **5b** only the first step is reversible (fig 3b). The voltammogram of compound **5c** in another solvent/electrolyte system, such as CH$_2$Cl$_2$/nBu$_4$NPF$_6$ 0.1 M, presents two closer oxidation peaks with half the intensity observed in MeCN/LiClO$_4$ (fig 4b); this phenomenon is probably due to a solvation effect of compound **5c**.

Table II. Oxidation peak potentials of tetrasubstituted dibenzothiophenes ($c = 2.5 \times 10^{-3}$ M) at a platinum microanode in MeCN/$LiClO_4$ 0.1 M; sweep rate = 100 mVs^{-1}; reference = Ag/Ag^+ 0.01 M.

Ep (V)	**5a** *2,8-NO$_2$-3,7-NMe$_2$*	**5b** *2,8-NMe$_2$-3,7-NH$_2$*	**5c** *2,3,7,8-NMe$_2$*
First step	0.68 (rev)	0.03 (rev)	0.14 (rev)
Second step	0.93 (rev)	0.35	0.66 (rev)



a b

Fig 3. Cyclic voltammetry ($v = 200$ mVs^{-1}) of 2,8-bis(dimethylamino)-3,7-dinitrodibenzothiophene **5a** (fig 3a) and 2,8-bis(dimethylamino)-3,7-diaminodibenzothiophene **5b** (fig 3b) ($c = 2.5$ mM in MeCN/$LiClO_4$ 0.1 M); Pt microanode; reference: Ag/Ag^+ 0.01 M in MeCN.

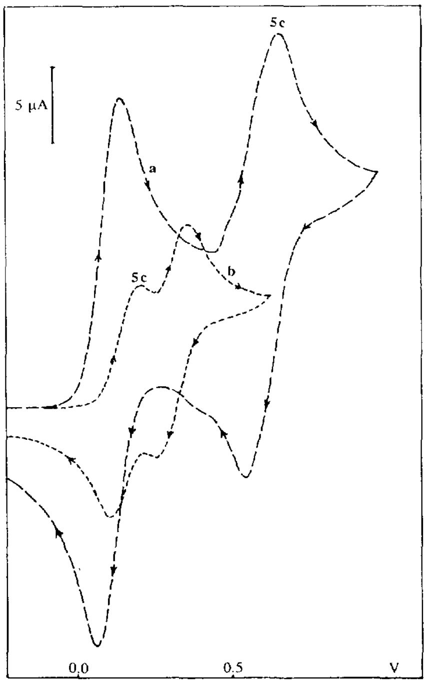


Fig 4. Cyclic voltammetry ($v = 100$ mVs^{-1}) of 2,3,7,8-tetrakis(dimethylamino)dibenzothiophene **5c** [$c = 2.5$ mM, in: a) MeCN/$LiClO_4$ 0.1 M, b) CH_2Cl_2/nBu_4NPF_6 0.1 M]; Pt microanode; reference: Ag/Ag^+ 0.01 M in MeCN.

Macroscale electrolyses

The preparative electrolyses were carried out in a three-compartment H-shaped cell, at a platinum foil anode (except in the cases of passivation where a graphite plate must be used) in MeCN/$LiClO_4$ 0.1 M with Ag/Ag^+ 10^{-2} M as a reference electrode.

The results for the electrooxidation of methoxylated dibenzothiophenes [1] suggested that the presence of at least two amino or dimethylamino substituents on dibenzothiophene are absolutely necessary for the preparation of a highly stable cation radical salt. However monoaminated dibenzothiophenes were subjected to anodic oxidation because their anodic behavior was unknown.

- *Electrooxidation of 2-aminodibenzothiophene* **1a**

The anodic oxidation of **1a**, in the presence of potassium carbonate as an insoluble base, led to a red compound which proved to be bis(dibenzothiophen-2-yl)diazene **6** (scheme 11).

The formation of diphenyldiazene (or azobenzene) was observed [17] previously by Wawzonek et al in the electrooxidation of aniline in acetonitrile, in the presence of a soluble base (such as pyridine); the following mechanism was proposed:

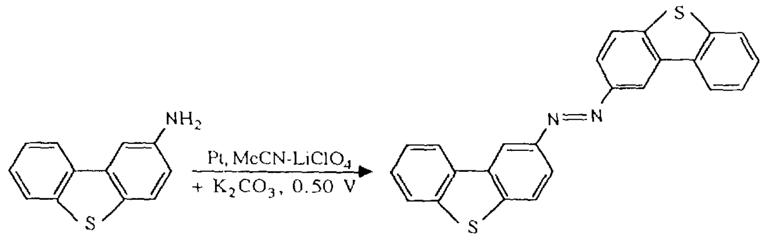
$$\text{Ar–NH}_2 \xrightarrow{-e^-} (\text{Ar–NH}_2)^{\cdot+} \xrightarrow{+\text{B}} \text{BH}^+ + \text{Ar–NH}^\cdot$$

$$2\ \text{Ar–NH}^\cdot \xrightarrow{\text{dim.}} \text{Ar–NH–NH–Ar} \xrightarrow{+2\text{B},\ -2e^-} 2\ \text{BH}^+ + \text{Ar–N} = \text{N–Ar}$$

- *Electrooxidation of 2-(dimethylamino)dibenzothiophene* **1b**

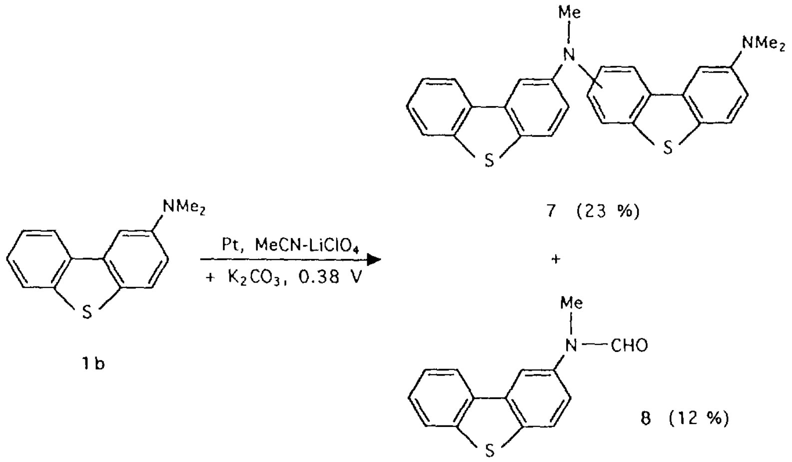
Among the numerous products formed in the anodic oxidation of 2-(dimethylamino)dibenzothiophene **1b**, in the presence of potassium carbonate, it was possible to isolate and identify coupling product **7** (formed by reaction of dimethylated amine **1b** with its monodemethylated derivative) and formamide **8**. To our knowledge, this is the first time that the formation of a formamide has been reported in the electrooxidation of an aromatic *N*,*N*-dimethylamine (scheme 12).

The formation of compound **7** involves a previously reported demethylation process of amine **1b** [18]. The electrooxidation of the demethylated amine generates a species that reacts with starting amine **1b** to give coupling product **7** according to the following mechanism [19]:



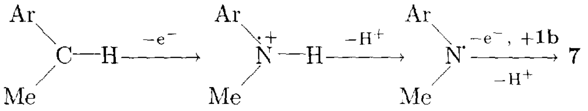
1a **6** (30 %)

Scheme 11



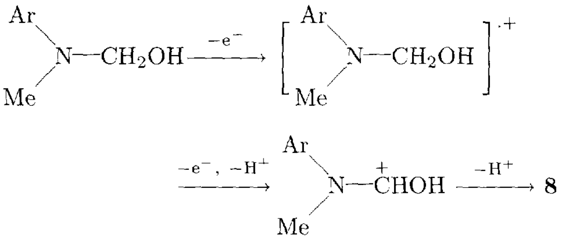
1b **7** (23 %) + **8** (12 %)

Scheme 12



$$\mathrm{Ar(Me)C{-}H} \xrightarrow{-e^-} \mathrm{Ar(Me)\overset{\cdot+}{N}{-}H} \xrightarrow{-H^+} \mathrm{Ar(Me)N^{\cdot}} \xrightarrow[-H^+]{-e^-,\ +1b} 7$$

Formamide **8** was formed via the *N*-hydroxymethylated derivative (intermediate of the demethylation reaction), part of which, instead of losing a molecule of methanol, was converted at the anode into an amide according to the sequence:



$$\mathrm{Ar(Me)N{-}CH_2OH} \xrightarrow{-e^-} \left[\mathrm{Ar(Me)N{-}CH_2OH}\right]^{\cdot+} \xrightarrow{-e^-,\ -H^+} \mathrm{Ar(Me)N{-}\overset{+}{C}HOH} \xrightarrow{-H^+} 8$$

- *Attempted electrooxidation of 3-aminodibenzothiophene* **3a**

It was not possible to carry out the anodic oxidation of amine **3a**, owing to a very strong passivation at platinum foil, and a graphite plate.

- *Electrooxidation of 3-(dimethylamino)dibenzothiophene* **3b**

As in the case of its isomer **1b**, the anodic oxidation of 3-(dimethylamino)dibenzothiophene **3b**, carried out in the presence of 2,6-lutidine, led to numerous products. It was possible to isolate and identify coupling product **9**, corresponding to product **7**, obtained from **1b**. A brown precipitate also formed which, according to mass spectrometry, possesses the same mass as diazene **6** minus one; unfortunately the insolubility of this product did not permit its identification (scheme 13).

- *Attempted electrooxidation of 2,8-diaminodibenzothiophene* **2a**

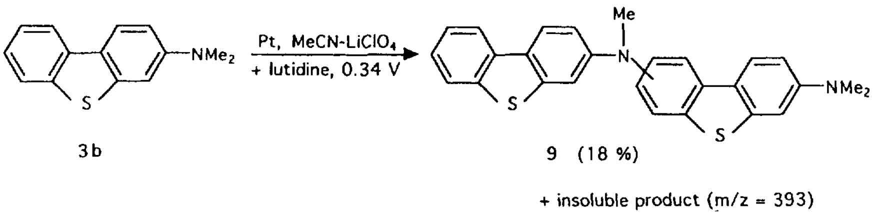
As in the case of 3-aminodibenzothiophene **3a**, it was not possible to oxidize anodically 2,8-diaminodibenzothiophene **2a**. There was total passivation at platinum foil, and a graphite plate, in neutral or acid medium.

- *Electrooxidation of 2,8-bis(dimethylamino)dibenzothiophene* **2b**

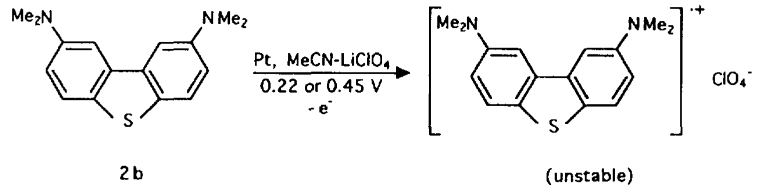
2,8-Bis(dimethylamino)dibenzothiophene **2b** exhibits two reversible oxidation peaks in cyclic voltammetry. Thus electrolyses were carried out, both at the potential of the first peak and at the potential of the second peak.

a) At the potential of the first peak

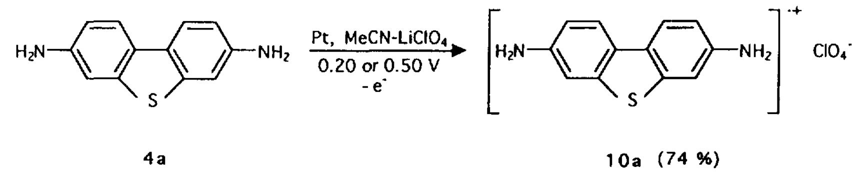
In MeCN/$LiClO_4$, at a potential of 0.22 V, a blue coloration typical of the formation of a cation radical appeared at a platinum anode, from a colorless starting solution. A UV-visible spectrum recorded during the



Scheme 13



Scheme 14



Scheme 15

electrolysis presented two absorption maxima at 460 and 880 nm. This cation radical was found to be unstable. At the end of the electrolysis, the electricity consumption was about one faraday per mole, and the deep blue color of the anolyte vanished progressively. A small amount of an unidentified precipitate was filtered off and, after usual work-up, only starting compound **2b** (50%) was recovered.

b) At the potential of the second peak

Under the same conditions as above, but now at a potential of 0.45 V, a deep purple solid formed as a deposit on the anode at the very beginning of the oxidation. However, after an electricity consumption of about one faraday per mole, the deposit began to disintegrate and finally vanished. At the end of the electrolysis the consumption was 1.5 faraday per mole. As above, the formation of the same small amount of precipitate was observed and the starting compound **2b** (30%) was isolated by chromatography (scheme 14).

An ESR spectrum registered during galvanostatic electrolyses of **2b**, in MeCN/LiClO$_4$ at a platinum anode with two different intensities (50 and 150 μA), confirmed the formation of the cation radical salt of **2b** (fig 5) which was unfortunately not stable enough to be isolated.

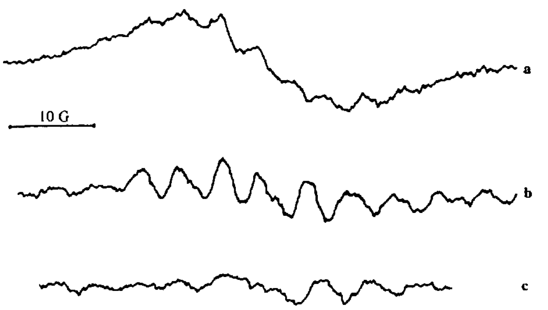
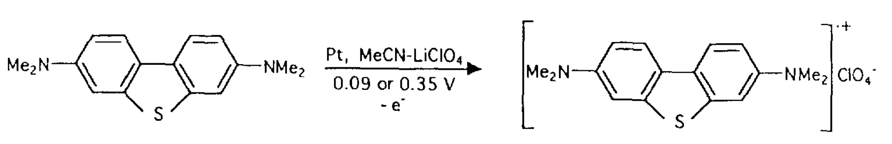


Fig 5. ESR signal attributed to the cation radical of 2,8-bis(dimethylamino)dibenzothiophene **2b**: a) during the electrooxidation of **2b** at a Pt microanode (in MeCN/LiClO$_4$ 0.1 M; i = 50 μA); b) in the same conditions, with i = 150 μA; c) after the end of the electrolysis.

• *Electrooxidation of 3,7-diaminodibenzothiophene* 4a

In MeCN/LiClO$_4$, the oxidation of **4a** at a platinum anode, carried out either at the potential of the first peak (+0.20 V) or at the potential of the second peak (+0.50 V) led, in both cases, to the deposit onto the anode of a blackish solid which proved to be **4a** cation radical perchlorate, namely 3,7-diaminodibenzothiophenium perchlorate **10a**, a stable product characterized by ESR spectroscopy (fig 6) and UV-visible spectroscopy (λ_{max} = 437, 532 and 854 nm). The ratio S/Cl determined by electron probe microanalysis was 52:48, confirming structure **10a** (one sulfur atom for one perchlorate anion) (scheme 15).

Another oxidation experiment, carried out in CH_2Cl_2/nBu$_4$NBF$_4$, at the potential of the first peak (0.20 V), allowed us to isolate cation radical tetrafluoroborate **4a** with an even better yield, 88%. This is probably due to a greater insolubity of the cation radical salt in dichloromethane.



4b **10b** (81 %)

Scheme 16

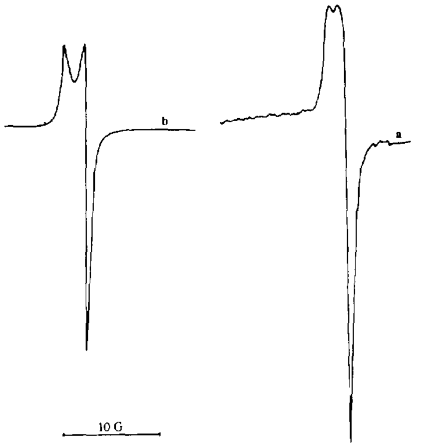


Fig 6. ESR spectra of the cation radical salt of 3,7-diaminodibenzothiophene **10a** recorded: a) during the electrooxidation of **4a** at a Pt microanode (in MeCN/$LiClO_4$ 0.1 M; i = 100 μA); b) in the solid state (powder).

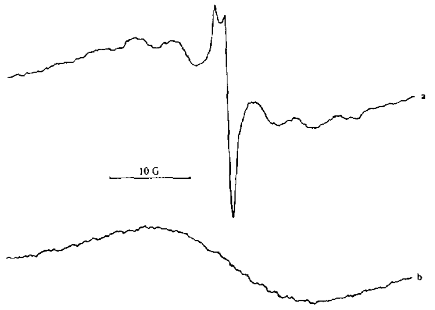


Fig 7. ESR spectra of the cation radical salt of 3,7-bis(dimethylamino)dibenzothiophene **10b** recorded: a) during the electrooxidation of **4b** at a Pt microanode (in MeCN/$LiClO_4$ 0.1 M; i = 80 μA); b) in the solid state (powder).

- *Electrooxidation of 3,7-bis(dimethylamino)dibenzothiophene* 4b

As above, the oxidation of compound **4b**, at a platinum anode, in MeCN/$LiClO_4$, carried out either at the potential of the first peak (+0.09 V) or the second peak (+0.35 V) led, in both cases, to the deposit onto the working electrode of a blue-green solid which proved to be **4b** cation radical perchlorate, namely 3,7-bis(dimethylamino)dibenzothiophenium perchlorate **10b**, also characterized by its ESR spectrum (fig 7). Compound **10b** was stable when kept in a desiccator but on exposure to air and moisture, it gradually (after several days) gave back starting compound **4b** (scheme 16).

■ *Spectroscopic and physical measurements*

A coulometric measurement of the electrooxidation of 3,7-bis(dimethylamino)dibenzothiophene **4b** in MeCN/$LiClO_4$ at a potential of 0.05 V confirmed the electricity consumption, already measured in preparative electrolysis, of 1 faraday per mole of starting substrate. Moreover, cyclic voltammetry carried out just at the end of the coulometry showed the complete disappearance of starting compound **4b**.

In UV-visible spectroscopy, the absorption maxima of the colorless solution of starting compound **4b** (λ_{max} = 200, 243, 311 and 348 nm) decreased during the electrolysis whereas other absorption maxima appeared: those of cation radical salt **10b** [λ_{max} = 418, 450, and 883–894 nm (broad and strong)]. However the molar extinction coefficients ε were not measurable since the major part of compound **10b** was insoluble and deposited onto the anode.

By reversing working electrode polarity, the electroreduction of compound **10b** (both the soluble part and the insoluble part) occurred. Then the UV-visible absorption maxima of compound **10b** disappeared progressively, and the maxima of compound **4b** reappeared simultaneously. Likewise a voltammogram registered after a few minutes of electroreduction of **10b** allowed us to see the reappearance of the oxidation peaks of **4b**.

The electrolysis of 3,7-diaminodibenzothiophene **4a** and 3,7-bis(dimethylamino)dibenzothiophene **4b**, in MeCN/$LiClO_4$, with a controlled intensity (100 μA for **4a** and 80 μA for **4b**), at a platinum gauze microanode, in a cell whose anodic compartment crosses the resonant cavity of an ESR spectrometer, permitted the recording of spectra which can be assigned with certainty to cation radicals salts **10a** and **10b** (fig 6a and 7a). In fact, these spectra were obtained at the very beginning of the electrolysis and underwent no modification of structure afterwards, during the continuation of the process. The ESR spectra of compounds **10a** and **10b**, in the solid state, were also recorded (fig 6b and 7b).

For the purpose of X-ray analysis, several attempts were carried out to prepare monocrystals of cation radical salts **10a** and **10b**, in a two-compartment H-shaped microcell. A platinum wire anode was used and a constant microcurrent applied at room temperature.

Despite numerous attempts in MeCN/$LiClO_4$ or CH_2Cl_2/$n$$Bu_4NClO_4$, compound **4b** gave no deposit onto the anode wire. Compound **4a** in MeCN/$LiClO_4$ gave a poorly crystallized deposit, but in CH_2Cl_2/$n$$Bu_4NClO_4$, with an intensity of 1 μA, it led to needles of cation radical perchlorate **10a** (see

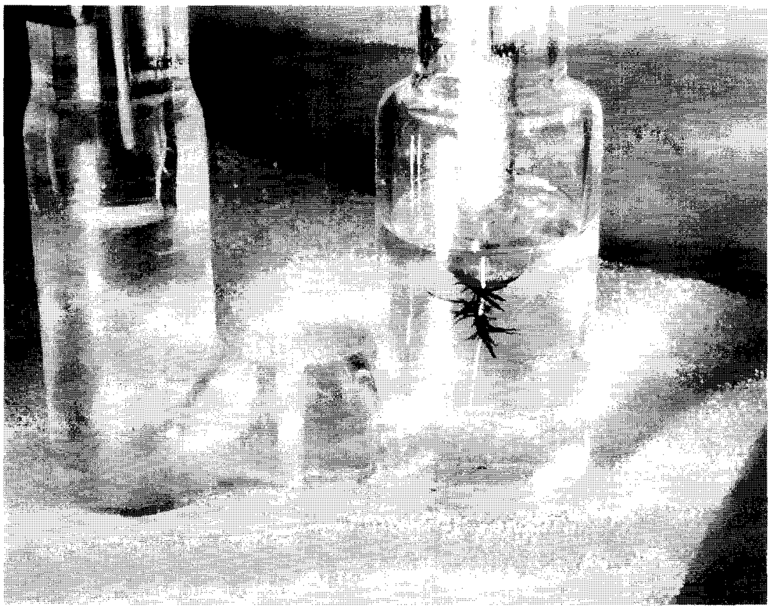


Fig 8. Photograph of the crystals of 3,7-diaminodibenzothiophenium perchlorate **10a**.

photograph; fig 8). However these needles proved to be twisted and consequently unusable for an X-ray structure determination.

- *Electrooxidation of 2,3,7,8-tetrakis(dimethylamino)dibenzothiophene* **5c**

Previously [1] we showed that, in the series of methoxylated dibenzothiophenes, 2,3,7,8-tetramethoxydibenzothiophene led, by anodic oxidation, to a stable cation radical salt. That is why we hoped that, in this series of aminated dibenzothiophenes, 2,3,7,8-tetrakis(dimethylamino)dibenzothiophene **5c**, with the same substituted positions and a reversible cyclic voltammogram, would also give a stable cation radical salt.

The oxidation of compound **5c**, at a platinum anode, in $MeCN/LiClO_4$, was carried out at 0.15 V, a value close to its first peak potential. At the outset, the anolyte was colorless and exhibited three UV absorption maxima (λ_{max} = 263, 304 and 343 nm). As soon as the electrolysis started the anolyte turned deep green; the recording of a UV-visible spectrum during the electrolysis showed the appearance of three absorption maxima (λ_{max} = 461, 826 and 884 nm). These maxima decreased after consumption of 1 faraday per mole whereas two new maxima (λ_{max} = 682 and 895 nm) started to appear when the consumption was close to 1.5 faraday per mole. At the end of the electrolysis, the consumption was 2 faradays per mole and there was no more absorption in the visible region.

The anolyte contained a scanty precipitate which proved to be the salt of amine **5c** with perchloric acid: $(\mathbf{5c}\text{-H})^+ClO_4^-$. After the usual work-up of the anolyte, chromatography of the residue allowed us to recover only a part of starting compound **5c** along with tarry matter.

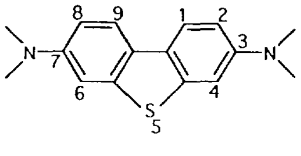
In the same conditions as above, but in the presence of 2,6-lutidine to neutralize the electrogenerated acidity, another attempt led only to the recovery of a part of the starting compound. Results were similar with another electrolyte such as $CH_2Cl_2/n\text{Bu}_4NPF_6$.

This failure to isolate the cation radical salt of **5c** must be correlated with the fact that only a very weak signal was observed in ESR spectroscopy during the electrooxidation of this compound.

Conclusion

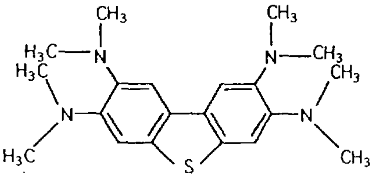
In the series of methoxylated dibenzothiophenes, it was concluded that the presence of two methoxy groups in the *ortho* position on each benzene ring was necessary to obtain stable cation radical salts [1].

In the present study, where the substituents on the dibenzothiophene are amino or dimethylamino groups, the conclusion is completely different. Actually the presence of only one substituent NH_2 or NMe_2 on each benzene ring is sufficient for stability of the cation radical formed. When both aminated groups are in the 3- and 7-positions, the stability of the cation radical is much higher than when these groups are in the 2- and 8-positions, and allows the chemical isolation. This is probably due to a better conjugation of the substituents in the 3- and 7-positions with the biphenyl system of dibenzothiophene (scheme 17).



Scheme 17

Paradoxically, the presence of two dimethylamino groups in the *ortho* position on each benzene ring of dibenzothiophene does not allow isolation of a stable cation radical salt. This can be explained by the steric hindrance between nearby NMe$_2$ groups which are markedly bulkier than OMe groups (scheme 18).



Scheme 18

Experimental section

General methods

The progress of reactions and the purity of samples were checked by TLC on silica gel plates (Merck no 5714). The purification of starting materials and electrolysis products was carried out by silica-gel column chromatography (Merck no 7736). The proton NMR spectra were recorded at 60 MHz, with TMS as an internal reference, in CDCl$_3$. Acetonitrile was purchased from Carlo-Erba, dried over molecular sieves (3 Å) and used without further purification. LiClO$_4$ was purchased from Fluka and kept in a desiccator.

Starting materials

- *2-Aminodibenzothiophene* **1a**

1a was prepared according to the procedure of Kudo et al [10]: reduction of 2-nitrodibenzothiophene [9] with hydrazine hydrate in the presence of palladium on carbon, in refluxing ethanol for 40 min: mp 132 °C (lit [10]: mp 132–133 °C).

- *2-(Dimethylamino)dibenzothiophene* **1b**

To a suspension of sodium hydrogenocarbonate (1.5 g) in water (5 mL) were added 2-aminodibenzothiophene **1a** (1.0 g, 4.9 mmol) and dimethyl sulfate (1.5 mL, 16 mmol). The mixture was stirred at room temperature until the reaction mixture became clear (about 30 min). Then it was heated at 60 °C until the end of effervescence (about 1 h). Afterwards 60% sodium hydroxide (10 mL) was added and the mixture was refluxed for 1 h. After cooling, dichloromethane was added; the solution was washed several times with water and dried over Na$_2$SO$_4$. After the usual work-up and purification of the residue by chromatography on silica gel (dichloromethane/cyclohexane 50:50), **1b** was isolated (oil, 0.904 g, 79%).

^{1}H NMR (CDCl$_3$, 60 MHz): δ NMe$_2$ 3.16 (s, 6H), δ Ar 6.90–8.10 (m, 7H).

MS (EI, 70 eV): m/z 229 (M$^+$).

- *3-Aminodibenzothiophene* **3a**

■ *Synthesis of dibenzothiophene oxide*

First, it was necessary to prepare an oxidizing reagent called UHP (urea-hydrogen peroxide) [20]: in a crystallizing dish, a solution of urea (6.0 g, 0.10 mol) in 30% hydrogen peroxide (12.9 mL, 0.15 mol) was warmed for a few minutes at 60 °C; the white crystals formed, after slow crystallization over 3 d, constituted the UHP reagent. Then the UHP reagent (4.50 g, 48 mmol) was added to a solution of phthalic anhydride (3.54 g, 24 mmol) in acetonitrile (40 mL). The resulting suspension was stirred for 15 min, then dibenzothiophene (2.21 g, 12 mmol) was added and the reaction mixture was stirred for 110 min (it is advisable to check the end of the reaction by TLC, with dichloromethane as an eluent, to minimize the formation of the sulfone at the expense of the sulfoxide).

After dilution with 40 mL water, the reaction mixture was saturated with solid sodium carbonate, extracted with dichloromethane, decanted off, washed several times with water and dried over Na$_2$SO$_4$. After the usual work-up and recrystallization in benzene, dibenzothiophene sulfoxide (1.80 g, 75%) was isolated: mp 180 °C (lit [12]: mp 180 °C).

■ *3-Nitrodibenzothiophene 5-oxide*

This compound was synthesized according to [13]: nitration by fuming nitric acid of an ice-cold mixture of dibenzothiophene sulfoxide with glacial acetic acid and concentrated sulfuric acid: mp 211 °C (ethanol).

■ *3-Aminodibenzothiophene* **3a**

3a was prepared according to the same authors [13]: reduction of 3-nitrodibenzothiophene 5-oxide, in glacial acetic acid, with a solution of stannous chloride in concentrated hydrochloric acid: mp 121 °C (ethanol).

- *3-(Dimethylamino)dibenzothiophene* **3b**

A suspension of sodium hydrogenocarbonate (3 g), water (10 mL), 3-aminodibenzothiophene **3a** (2.0 g, 9.8 mmol) and dimethyl sulfate (3 mL, 32 mmol) was stirred at room temperature until the reaction mixture cleared. Then it was heated to 60 °C until the end of effervescence (about 1 h). Afterwards 60% sodium hydroxide (20 mL) was added and the mixture was refluxed for 1 h. After cooling, the mixture was extracted by dichloromethane, decanted off, washed several times with water and dried over Na$_2$SO$_4$. After the usual work-up and purification of the residue by chromatography on silica gel (cyclohexane/dichloromethane, 75:25), **3b** (1.80 g, 80%) was isolated: mp 140–141 °C (methanol).

^{1}H NMR (CDCl$_3$, 60 MHz): δ NMe$_2$ 3.05 (s, 6H), δ Ar 6.86–8.05 (m, 7H).

Anal calc for C$_{14}$H$_{13}$NS: C, 73.34; H, 5.70; N, 6.10; S, 13.98. Found: C, 73.62; H, 5.78; N, 6.32; S, 14.12.

- *2,8-Diaminodibenzothiophene* **2a**

A suspension of 2,8-dinitrodibenzothiophene (2.70 g, 9.8 mmol), prepared according to [11], and 10% Pd-C catalyst in ethanol (800 mL) was warmed to 60 °C. Then a solution of hydrazine hydrate (50 mL) in ethanol (200 mL) was added and the mixture was refluxed for 90 min. After removal of the catalyst by filtration and ethanol by distillation, recrystallization of the residue in ethanol gave diamine **2a** (0.81 g, 38%): mp 201 °C (lit [11]: mp 194–196 °C).

- *2,8-Bis(dimethylamino)dibenzothiophene* **2b**

A mixture of sodium hydrogenocarbonate (2.5 g), water (8.5 mL), 2,8-diaminodibenzothiophene **2a** and dimethyl sulfate (2.7 mL, 25.8 mmol) was stirred at room temperature for 1 h and warmed to 60 °C for 1 h. Then 60% sodium hydroxide (20 mL) was added and the mixture refluxed for 2 h. After cooling the mixture was extracted with dichloromethane, decanted off, washed several times with water and dried over Na$_2$SO$_4$. After the usual work-up and recrystallization of the residue in methanol, diamine **2b** was isolated: mp 160 °C.

UV (ethanol), λ_{max} (ε): 204.5 (22000), 247 (51700), 257.5 (43300), 270.5 (30500), 283 (20200), 332.5 (8600), 378.5 (2800) nm.

^{1}H NMR (CDCl$_3$, 60 MHz): δ NMe$_2$ 3.05 (s, 12H), δ Ar 6.83–7.76 (m, 6H).

MS (EI, 70 eV): m/z 270 (M^+).

Anal calc for $C_{16}H_{18}N_2S$: C, 70.07; H, 6.70; N, 10.36; S, 11.85. Found: C, 70.50; H, 6.69; N, 10.46; S, 11.89.

• *3,7-Diaminodibenzothiophene* **4a**

4a was prepared according to [14]: reduction of a suspension of 3,7-dinitrodibenzothiophene-5-oxide in glacial acetic acid with stannous chloride in concentrated hydrochloric acid: mp 169 °C (lit [14]: mp 169–170 °C).

• *3,7-Bis(dimethylamino)dibenzothiophene* **4b**

4b was prepared by the same method as **2b** (yield: 85%), mp 241 °C (methanol).

UV (ethanol), λ_{max} (ε): 200 (22300), 243 (42100), 311 (33100), 348 (18300) nm.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 3.01 (s, 12H), δ Ar 6.90 (dd, 2-H and 8-H, J_{ortho} = 8 Hz, J_{meta} = 3 Hz)and 7.86 (d, 1-H and 9-H, J_{meta} = 8 Hz).

MS (EI, 70 eV): m/z 270 (M^+).

Anal calc for $C_{16}H_{18}N_2S$: C, 71.07; H, 6.70; N, 10.36; S, 11.85. Found: C, 70.37; H, 6.71; N, 10.21; S, 11.98.

• *2,8-Bis(dimethylamino)-3,7-dinitrodibenzothiophene* **5a**

■ *Synthesis of 2,8-dibromo-3,7-dinitrodibenzothiophene 5-oxide*

This compound was prepared according to [16]: dinitration of 2,8-dibromodibenzothiophene [15] by fuming nitric acid: mp 294 °C (lit [16]: mp 283–292 °C).

■ *Synthesis of 2,8-dibromo-3,7-dinitrodibenzothiophene*

A solution of 2,8-dibromo-3,7-dinitrodibenzothiophene-5 oxide (5.0 g, 11.6 mmol) and *tert*-butyl bromide in dioxane (150 mL) was heated at 80 °C, for 24 h. After cooling, the reaction mixture was poured onto ice. The filtration and recrystallization of the precipitate gave 2,8-dibromo-3,7-dinitrodibenzothiophene (3.6 g, 77%): mp 256 °C.

IR (KBr): ν NO_2 1 345 and 1 515 cm^{-1} (no SO band).

MS (EI, 70 eV): m/z 430 (M^+).

■ *2,8-Bis(dimethylamino)-3,7-dinitrodibenzothiophene* **5a**

■ *a) By reaction with hexamethylphosphoramide (HMPA)*

Under a nitrogen atmosphere, a solution of 2,8-dibromo-3,7-dinitrodibenzothiophene (3.0 g, 7 mmol) in hexamethylphosphoramide (20 mL) was heated, on a metallic bath, at 175 °C, for 16 h. A deep red color appeared. After cooling the reaction mixture was diluted with ether/ethyl acetate, washed several times with water (in order to completely remove HMPA) and dried over Na_2SO_4. After the usual work-up, the residue was purified by column chromatography on silica gel (cyclohexane/dichloromethane 50:50) to give **5a** (2.0 g, 80%): mp 242–244 °C (methanol/acetone).

UV-visible (ethanol), λ_{max} (ε): 203 (12700), 212 (12800), 269 (14700), 328 (10100), 501 (1600) nm.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 2.99 (s, 12H), δ Ar 7.21 (s, 1-H and 9-H) and 8.23 (s, 4-H and 6-H).

MS (EI, 70 eV): m/z 360 (M^+).

■ *b) By reaction with dimethylammonium chloride*

Under a nitrogen atmosphere, a mixture of 2,8-dibromo-3,7-dinitrodibenzothiophene (2.0 g, 4.6 mmol) in pyridine (14 mL) with sodium hydrogenocarbonate (2.3 g) and dimethylammonium chloride (1.4 g) in water (1 mL) was heated at reflux for 20 h. A deep red color appeared. After cooling, the reaction mixture was diluted with ether/ethyl acetate, washed several times with water and dried over Na_2SO_4. After the usual work-up, the residue was purified as above to give **5a** (1.0 g, 65%).

• *2,8-Bis(dimethylamino)-3,7-diaminodibenzothiophene* **5b**

To a solution of 2,8-bis(dimethylamino)-3,7-dinitrodibenzothiophene **5a** (2.0 g, 5.55 mmol) in ethanol (700 mL), with 10% Pd-C catalyst (1.5 g), warmed to 60 °C, was added a solution of hydrazine hydrate (40 mL) in ethanol (200 mL). The reaction mixture was refluxed for 75 min. After cooling, the Pd-C catalyst was filtered off and ethanol was evaporated off. The residue was purified by column chromatography on silica gel (cyclohexane/dichloromethane 25:75) to give **5b** (0.5 g, 30%): mp 150 °C.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 2.78 (s, 12H), δ NH_2 4.06 (broad, 4H), δ Ar 7.11 (s, 2H) and 7.61 (s, 2H).

MS (EI, 70 eV): m/z 300 (M^+).

• *2,3,7,8-Tetrakis(dimethylamino)dibenzothiophene* **5c**

A mixture of sodium hydrogenocarbonate (6.875 g), water (25 mL), 2,8-bis(dimethylamino)-3,7-diaminodibenzothiophene **5b** (2.5 g, 8.33 mmol) and dimethyl sulfate (7.5 mL, 80 mmol) was stirred, at room temperature for 1 h and warmed to 60 °C for 45 min. Then 60% sodium hydroxide (50 mL) was added and the reaction mixture was refluxed for 2 h. After cooling, the mixture was extracted by dichloromethane, decanted off, washed several times with water and dried over Na_2SO_4. After the usual work-up, the residue was purified by chromatography on silica gel (cyclohexane/triethylamine 95:5) to give tetraamine **5c** (2.0 g, 66%): mp 160 °C (methanol).

UV-visible (ethanol), λ_{max} (ε): 263 (43900), 304 (12300), 343 (22200) nm.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 2.86 (s, 24H), δ Ar 7.28 (s, 2H) and 7.51 (s, 2H).

MS (EI, 70 eV): m/z 356 (M^+).

Anal calc for $C_{20}H_{48}N_4S$: C, 67.31; H, 7.90; N, 15.70; S, 8.99. Found: C, 66.93; H, 7.83; N, 15.74; S, 9.02.

Macroscale electrolyses

Macroscale electrooxidations were carried out at room temperature, without bubbling inert gas, in a three-compartment H-shaped cell. The intermediate compartment (useful volume: 5 mL) was used to minimize the mixing of the catholyte (V: 30 mL) and anolyte (V: 65 mL); the compartments were separated by two glass-frits (inside diameter: 2 cm). The anode was a platinum foil (area: 4 × 4 cm), the cathode a graphite rod (diameter: 1 cm) and reference electrode Ag/Ag^+ 0.01 M in MeCN. A volume of 100 mL $MeCN/LiClO_4$ 0.1 M was divided among the three compartments and salt bridge. Between 1 and 2 mmol aminated dibenzothiophene was added to the anodic compartment which was closed by a silicone stopper. When the presence of a base was required, 2,6-lutidine or potassium carbonate was added to the anolyte. The electrolysis was continued until the intensity dropped to zero.

• *Anodic oxidation of 2-aminodibenzothiophene* **1a**

Compound **1a** (199 mg, 1 mmol) was oxidized at a platinum anode, in $MeCN/LiClO_4$ 0.1 M in the presence of potassium carbonate (0.50 g), at a potential of 0.50 V, for 8 h. The electricity consumption was 1 faraday per mole. The anolyte was diluted with dichloromethane (150 mL) and water (150 mL), decanted off, washed with water

(4 × 50 mL) and dried over Na_2SO_4. After the usual work-up, the residue was purified by chromatography on silica gel (dichloromethane/cyclohexane 50:50) to give, along with recovered starting material **1a** (45 mg), a red compound, bis(dibenzothiophen-2-yl) **6** (60 mg, 30%): mp 240 °C (MeCN).

IR (KBr): ν N=N 1 580 cm^{-1} (weak).

NMR: the poor solubility in the usual NMR solvents did not allow us to obtain a usable spectrum.

MS (EI, 70 eV): m/z 394 (M^+).

• *Anodic oxidation of 2-(dimethylamino)dibenzothiophene* **1b**

Compound **1b** (229 mg, 1 mmol) was oxidized at a platinum anode, in $MeCN/LiClO_4$ 0.1 M in the presence of potassium carbonate (0.50 g), at a potential of 0.38 V for 24 h. The electricity consumption was 2 faradays per mole. The anolyte was then diluted with dichloromethane (150 mL) and water (150 mL), decanted off, washed with water (4 × 50 mL) and dried over Na_2SO_4. After the usual work-up, the residue was purified by chromatography on silica gel (dichloromethane/cyclohexane 50:50) to give, along with recovered starting compound **1b** (55 mg) and a mixture of unidentified products (30 mg), a coupling product, namely 7(or 8)-[dibenzothiophen-2-yl(methyl)amino]-2-(dimethylamino)dibenzothiophene **7** (50 mg, 23%), and (*N*-methyl-*N*-(dibenzothiophen-2-yl)methanamide **8** (30 mg, 12%).

7: mp 204 °C.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 2.66 (s, 6H), δ NMe 3.52 (s, 3H), δ Ar 6.63–8.10 (m, 13H).

MS (EI, 70 eV): m/z 438 (M^+).

8: mp 78 °C.

IR (KBr): ν CHO 1 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ NMe 3.43 (s, 3H), δ Ar 7.26–8.23 (m, 7H), δ N-CHO 8.61 (s, 1H).

MS (EI, 70 eV): m/z 241 (M^+).

• *Attempted anodic oxidation of 3-aminodibenzothiophene* **3a**

When **3a** (199 mg, 1 mmol), in $MeCN/LiClO_4$ 0.1 M in the presence of potassium carbonate (1.0 g), was subjected to anodic oxidation at a potential of 0.45 V, at either platinum foil or a graphite plate, total passivation was observed.

• *Anodic oxidation of 3-(dimethylamino)dibenzothiophene* **3b**

Compound **3b** (343 mg, 1.5 mmol) was oxidized at a platinum anode, in $MeCN/LiClO_4$ 0.1 M, in the presence of 2,6-lutidine (0.35 mL, 3 mmol), at a potential of 0.34 V, for 22 h. The electricity consumption was 2 faradays per mole. First, an unidentified brown insoluble matter [50 mg, MS: m/z 393 (M^+)] was filtered off. Then the filtrate was diluted with dichloromethane (150 mL) and water (150 mL), decanted off, washed with water (4 × 50 mL) and dried over Na_2SO_4. After the usual work-up, the residue was purified by chromatography on silica gel (dichloromethane/cyclohexane 50:50) to give a coupling product, 7(or 8)-[dibenzothiophen-3-yl(methyl)amino]-3-(dimethylamino)dibenzothiophene **9** (60 mg, 18%): mp 240 °C.

^1H NMR ($CDCl_3$, 60 MHz): δ NMe_2 2.85 (s, 6H), δ NMe 3.40 (s, 3H), δ Ar 6.70–8.13 (m, 13H).

MS (EI, 70 eV): m/z 438 (M^+).

• *Attempted anodic oxidation of 2,8-diaminodibenzothiophene* **2a**

When **2a** (214 mg, 1 mmol), in $MeCN/LiClO_4$ 0.1 M, was subjected to anodic oxidation at a potential of 0.35 V, total passivation was observed not only at a platinum foil, but also at a graphite plate.

• *Anodic oxidation of 2,8-bis(dimethylamino)-dibenzothiophene* **2b**

When **2b** (270 mg, 1 mmol), in $MeCN/LiClO_4$ 0.1 M was oxidized at a platinum anode:

– at a potential of 0.22 V, a blue coloration appeared first, then decreased markedly at the end of the electrolysis;

– at a potential of 0.45 V, a deep purple solid deposited onto the anode, then disintegrated progressively and disappeared completely at the end of the electrolysis.

After work-up of the anolyte, only the starting compound **2b** was recovered: 50% in the first case and 30% in the second case.

• *Anodic oxidation of 3,7-diaminodibenzothiophene* **4a**

■ *a) In $MeCN/LiClO_4$*

Compound **4a** (321 mg, 1.5 mmol) was oxidized, at a platinum anode in $MeCN/LiClO_4$ 0.1 M, at a potential of 0.20 V for 15 h (another run, at a potential of 0.50 V, led to the same result). The electricity consumption was about 1 faraday per mole. Blackish crystals deposited progressively onto the anode. They were filtered off, washed with dry acetonitrile (3 × 1 mL) and dried in air. Thus 3,7-diaminodibenzothiophenenium perchlorate **10a** (350 mg, 74%) was isolated: mp 268 °C (decomposition).

IR (KBr): ν ClO_4^- 1 090 cm^{-1}.

UV-visible: λ_{max} 437, 532 and 854 nm.

ESR: see theoretical part.

Anal: $(C_{12}H_{10}N_2S)_x \cdot ClO_4$.

The S/Cl ratio determined by electron probe microanalysis was 52:48, ie, $x \approx 1.1$;

By elemental analysis, it was found for $x = 1.35$ that the calculated percentages were closest to the found values: calc: C, 50.18; H, 3.15; Cl, 8.89; N, 9.76; O, 16.50; S, 11.16. Found: C, 51.66; H, 3.58; Cl, 9.00; N, 9.57; O, 15.06; S, 11.15.

Given the difficulties of the elemental analysis of this type of compound, it is the S/Cl ratio determined by electron probe microanalysis which seems to be the most reliable.

■ *b) In CH_2Cl_2/nBu_4NBF_4*

Under the same conditions as above, but in CH_2Cl_2/nBu_4 NBF_4 0.1 M (instead of $MeCN/LiClO_4$ 0.1 M), **4a** (321 mg, 1.5 mmol) was oxidized at the same potential of 0.20 V for 15 h. The electricity consumption was about 1 faraday per mole. Blue-black crystals deposited onto the anode progressively. They were filtered off, washed with dry dichloromethane (3 × 1 mL) and dried in air. Thus 3,7-diaminodibenzothiophenium tetrafluoroborate **10a′** was isolated: mp 250 °C (pasty).

IR (KBr): ν BF_4^- 1 030–1 060 cm^{-1}.

Anal: $(C_{12}H_{10}N_2S)_x$ BF_4.

For $x = 52/48 \approx 1.1$, the value determined by electron probe microanalysis for compound **10a**, the calculated percentages are the closest to the found percentages, except for boron and fluorine presenting an important discrepancy, probably due to a loss of BF_3 at the time of the combustion of the sample; in fact, the sum of the percentages of the analyzed elements is only 91.34%.

Anal calc: C, 49.00; H, 3.42; N, 9.52; S, 10.89; B, 3.39; F, 23.83. Found: C, 48.98; H, 3.63; N, 9.45; S, 11.00; B, 2.50; F, 15.78.

- *Anodic oxidation of 3,7-bis(dimethylamino) dibenzothiophene* **4b**

Compound **4b** (270 mg, 1 mmol) was oxidized at a platinum anode in MeCN/$LiClO_4$ 0.1 M, at a potential of 0.09 V for 22 h (another run at a potential of 0.35 V led to the same result). The electricity consumption was about 1 Faraday per mole. Blue-green crystals deposited progressively onto the anode. They were filtered off, washed with dry acetonitrile (3 × 1 mL) and dried in air. Thus 3,7-bis(dimethylamino)dibenzothiophenium perchlorate **10b** (270 mg, 75%) was isolated: mp 150–190 °C (pasty).

IR (KBr): ν ClO_4^- 1 090 cm^{-1}.

UV-visible: λ_{max} 418, 450 and 880 (broad) nm.

ESR: see theoretical part.

Anal calc for $C_{16}H_{18}N_2SClO_4$: C, 52.01; H, 4.91; N, 7.58; S, 8.67; Cl, 9.59; O, 17.32. Found: C, 50.56; H, 5.00; N, 7.29; S, 9.30; Cl, 9.42; O, 18.20.

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