Unexpected electrochemical behaviour of highly bulky aromatic hexasulfones

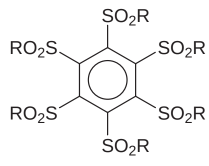
Conformational change under electron transfer

Ahmed Ghanimi, Bruno Fabre and Jacques Simonet*

Laboratoire d'Electrochimie Moléculaire et Macromoléculaire (CNRS UMR 6510), Campus de Beaulieu, Université de Rennes 1, 35042 Rennes cédex, France

A series of hexa(alkylsulfonyl)benzenes were studied electrochemically in aprotic media at a platinum electrode. It was found that the voltammetric behaviour strongly depends on the bulkiness of the alkyl groups as well as on parameters like temperature and/or sweep rate. It is pointed out that the title compounds can exist in two forms possessing quite different standard potentials. The ratio between these two structures is strongly influenced by an inner structure reorganization following electron transfer.

The specific activation of molecules by alkyl- and aryl-sulfonyl groups is now a well-documented area.[1–9] During at least the last two decades, special attention has been paid to the activation of aromatic compounds by one or more sulfonyl groups as substituents and the cathodic behaviour of aromatic sulfones was found to be strongly modified as the substituents became larger and larger. Thus, increased stabilization of anion radicals relative to such structures, together with a progressive increase of their standard potentials, have been observed. More specifically, aromatic sulfones lead cathodically to anion radicals whose formation potential, as well as lifetime, depend strongly on their π^* level, that is the number and the nature of electron-withdrawing groups directly bonded to the aromatic ring.



1a: R = Methyl
1b: R = Ethyl
1c: R = *n*-Propyl
1d: R = *n*-Butyl
1e: R = *n*-Hexyl
1f: R = *n*-Octyl
1g: R = *iso*-Propyl
1h: R = *iso*-Butyl
1i: R = Benzyl

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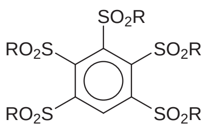

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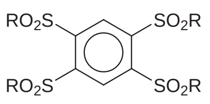

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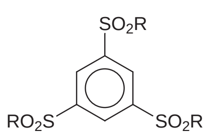

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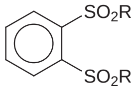

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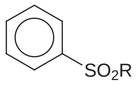

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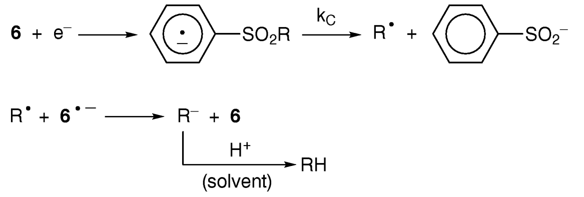
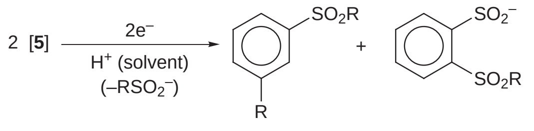
Thus, among the rather wide palette of mono- and polysulfones, it has been especially reported that sulfones **3**–**6** present rather amazing cathodic behaviour. It is now well-established that phenylalkylsulfones **6** are reduced[2] in aprotic organic media at about -1.2 V *vs.* SCE (reduction potential weakly depending on the nature of R) to afford a radical anion, which was shown to be cleaved last as noted opposite.

The cleavage rate constant k_c at room temperature was estimated[3] to be of the order of 10^5 s^{-1} (R = methyl) justifying the disproportionation (disp.) mechanism given above.

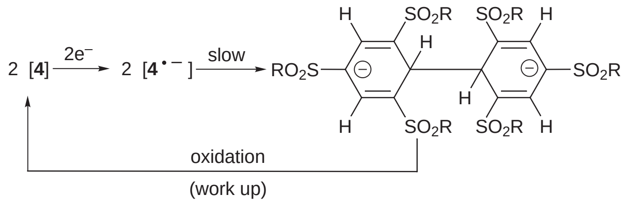


From these considerations, the cathodic reduction of **5** was found to be totally unexpected,[5,9] since the process corresponds globally to a 'self' alkylation, which can be described by the following equation:



The radical alkylation process goes through the formation of a transient R•, issued from the decomposition of the anion radical $5^{\bullet -}$ followed by a radical coupling.

Even more surprisingly, the cathodic reduction of trisulfones **4** is still different from those occurring with mono- and di-sulfones since the relevant anion radical, although very stable, was found[6–8] to dimerize. The transient formation of a dianion, by coupling, was demonstrated[7,8] by *in situ* ^{1}H and ^{13}C NMR of the catholyte and its structure depends on the nature of R. The chemically reversible process in the absence of acid, with R = Pr^i, can be written as follows:



Now, the tetrasulfones **3**[4] and pentasulfones **2**[10] (checked to be strong π acceptors) can all be reversibly reduced into both the highly stabilized anion radical and dianion. The first cathodic peak remains reversible even upon lowering the temperature and/or increasing the sweep rate, showing therefore that any coupling—even reversible—cannot be considered. It is important to specify that within the time scale of the cyclic voltammetry, formation of the dimer dianionic form has not been observed (dimerization rate constant k_c at room temperature can be estimated to be less than 2×10^{-2} s^{-1}). However, very slow irreversible coupling reactions afforded polyalkyl- or polyaryl-sulfonyl biphenyls.[10]

Additionally, the cleavage reaction was shown to take place only at the dianion level (protonation of the electrogenerated dibasic form, followed by elimination of a sulfinate ion, restores aromaticity).

We now wish to report experimental data concerning a hexasulfonyl benzenes series such as **1a**–**i**. Do these compounds show even greater π-acceptor properties than those already reported with tri-, tetra- and even bulky pentasulfones? What is the influence of the large substituent bulk on the orientation of the product distribution? In other words, do we favour either cleavage or dimerisation? And especially, what is the influence of hindrance on the standard potential $E°$, corresponding to the first heterogeneous electron transfer, and is this potential always specific to the planar structure of **1**?

The present paper aims to answer these questions and demonstrate that, in some cases strongly dependent on the structure of the R groups, two redox systems can be found with hexasulfones **1**. The consequences of these internal energy changes taking place during electron transfer are discussed below.

Experimental

Substrate synthesis

All substrates **1** were prepared according to a method already reported in the literature,[11–14] which consists first in the preparation of poly(alkylthio)benzenes and then in oxidizing them by *m*-chloroperbenzoic acid. (In the following, all NMR chemical shifts are given *versus* TMS and coupling constants in Hz.) **1a**. Hexa(methylsulfonyl)benzene (reported in ref. 17): mp > 280 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 6 × CH_3). **1b**. Hexa(ethylsulfonyl)benzene (previously unknown): mp > 280 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.30 (q, 6 × CH_2, $^3J_{HH} = 7.60$); 1.50 (t, 6 × CH_3, $^3J_{HH} = 7.60$). **1c**. Hexa(propylsulfonyl)benzene (previously unknown): mp > 280 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.23 (t, 6 × CH_2, $^3J_{HH} = 7.69$); 2.00–2.12 (m, 6 × CH_2); 1.16 (t, 6 × CH_3, $^3J_{HH} = 7.47$). **1d**. Hexa(butylsulfonyl)benzene (previously unknown): mp 175–176 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.30 (t, 6 × CH_2, $^3J_{HH} = 7.80$); 1.91–2.12 (m, 6 × CH_2); 1.40–1.60 (m, 6 × CH_2); 1.02 (t, 6 × CH_3, $^3J_{HH} = 7.20$). **1e**. Hexa(hexylsulfonyl)benzene (reported in ref. 18): mp 167 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.20 (t, 6 × CH_2, $^3J_{HH} = 7.70$); 1.90–2.10 (m, 6 × CH_2); 1.40–1.60 [m, 6 × $(CH_2)_3$]; 1.02 (t, 6 × CH_3, $^3J_{HH} = 6.80$). **1f**. Hexa(octylsulfonyl)benzene (reported in ref. 18): mp 136 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.20 (t, 6 × CH_2, $^3J_{HH} = 7.80$); 1.90–2.10 (m, 6 × CH_2); 1.20–1.50 [m, 6 × $(CH_2)_5$]; 1.02 (t, 6 × CH_3, $^3J_{HH} = 6.70$). **1g**. Hexa(isopropylsulfonyl)benzene (previously unknown): mp > 280 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.50–4.70 (m, 6H); 1.80 (d, 4 × CH_3, $^3J_{HH} = 6.60$); 1.50 (d, 4 × CH_3, $^3J_{HH} = 6.60$); 0.90 (d, 4 × CH_3, $^3J_{HH} = 6.20$). **1h**. Hexa(isobutylsulfonyl)benzene (previously unknown): mp 162 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.10–4.20 (m, 6H); 2.10–2.30 (m, 2 × CH_2); 1.70–1.90 (m, 3 × CH_2); 1.50 (d, 6 × CH_3, $^3J_{HH} = 6.10$); 1.10 (t, 6 × CH_3, $^3J_{HH} = 6.90$) **1i**. Hexa(benzylsulfonyl)benzene (previously unknown): mp > 300 °C (CH_2Cl_2–EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.70 (m, 30H); 5.76 and 5.53 (AB system, 3 × CH_2, $J_{AB} = 12.91$); 4.87 and 4.45 (AB system, 3 × CH_2, $J_{AB} = 12.96$). The preparative scale electrochemical reduction of **1c**, **1d** and **1f** allowed the pentasulfone derivatives **2** to be isolated.

2a. Penta(propylsulfonyl)benzene: mp 208 °C (EtOH). ^1H NMR (300 MHz, $CDCl_3$): δ 9.07 (s, ArH); 4.22–4.29 (m, 3 × CH_2); 4.13–4.18 (m, 2 × CH_2); 2.04–2.14 (m, 5 × CH_2); 1.15–1.18 (m, 5 × CH_3). **2b**. Penta(butylsulfonyl)benzene: mp 207–208 °C (EtOH). ^1H NMR (200 MHz, $CDCl_3$): δ 9.1 (s, ArH); 4.1–4.4 (m, 3 × CH_2); 3.6–3.8 (m, 2 × CH_2); 1.8–2.2 (m, 5 × CH_2); 1.4–1.7 (m, 5 × CH_2); 0.9–1.1 (m, 5 × CH_3). **2c**. Penta(octylsulfonyl)benzene: mp 94–95 °C (EtOH). ^1H NMR (200 MHz, $CDCl_3$): δ 9.1 (s, ArH); 4.1–4.4 (m, 3 × CH_2); 3.7–3.9 (m, 2 × CH_2); 2.0–2.2 (m, 5 × CH_2); 1.2–1.6 [m, 5 × $(CH_2)_5$]; 0.8–1.0 (m, 5 × CH_3).

Electrochemical measurements

All the electroanalytical investigations were carried out in a one-compartment glass cell containing 0.1 M NBu_4BF_4 in dimethylformamide (DMF) as the supporting electrolyte (volume: 7 ml).

An EGG PAR Model 173 potentiostat monitored with an EGG PAR Model 175 signal generator was used in the standard three-electrode configuration to control reduction potentials in cyclic voltammetry. All potentials are referred to a Ag/AgI/0.1 M NBu_4I system in DMF. A platinum disk (diameter: 1 mm) was used as the working electrode and the counter electrode was a glassy carbon rod. The cyclic voltammetry traces were plotted on an XY SEFRAM-type TGM 164 recorder.

For scan rate values higher than 0.5 V s^{-1}, the solution resistance was compensated by positive feedback. The ferrocene/ferrocenium couple served as an internal standard and its reversible potential in DMF + 0.1 M NBu_4BF_4 is 0.960 V *vs.* Ag | AgI | 0.1 MI^- at room temperature.

Preparative electrolysis experiments were performed using a Tacussel potentiostat/galvanostat type PJT 120-1. A U-shaped two-compartment cell was used and the working electrode was a rectangular platinum sheet.

Tetrabutylammonium tetrafluoroborate, purchased from Fluka, was recrystallized three times from a 1 : 1 methanol : water mixture and then carefully dried under vacuum for 48 h.

DMF from SDS was verified to contain less than 50 ppm of water and then was used without further purification.

Spectroscopic analyses

EPR spectra were recorded on a Bruker ER 200 D spectrometer. The radical anions of hexasulfones were electrolytically produced directly within the EPR machine cavity. ^1H NMR spectra of sulfones were obtained on a Bruker AC 300P spectrometer.

Results

Molecular structure

The structure of the bulky hexasulfones was determined by X-ray crystallography. Thus, crystal data {9639 measured reflections, 4044 observed reflections [$I > 3\sigma(I)$], μ (Mo-Kα) = 3.045 cm^{-1}, $F(000) = 1044$, $T = 293$ K} for the hexyl derivative **1e** at room temperature was refined in the space group $P1$ with two molecules per unit cell. The crystal is triclinic; $a = 10.005(2)$ Å, $b = 16.61(1)$ Å, $c = 17.70(1)$ Å; $\alpha = 112.31(7)°$; $\beta = 99.91(9)°$; $\gamma = 100.70(9)°$ and $U = 2586(6)$ Å^3; $D = 1.42$ g cm^{-3}. Final R values were 0.063 ($R_w = 0.060$).

The structure of **1e** is shown in Fig. 1. The benzene ring is clearly distorted, and the six SO_2 groups are located alternately up and down from the 'plane' of the benzene ring. Thus,

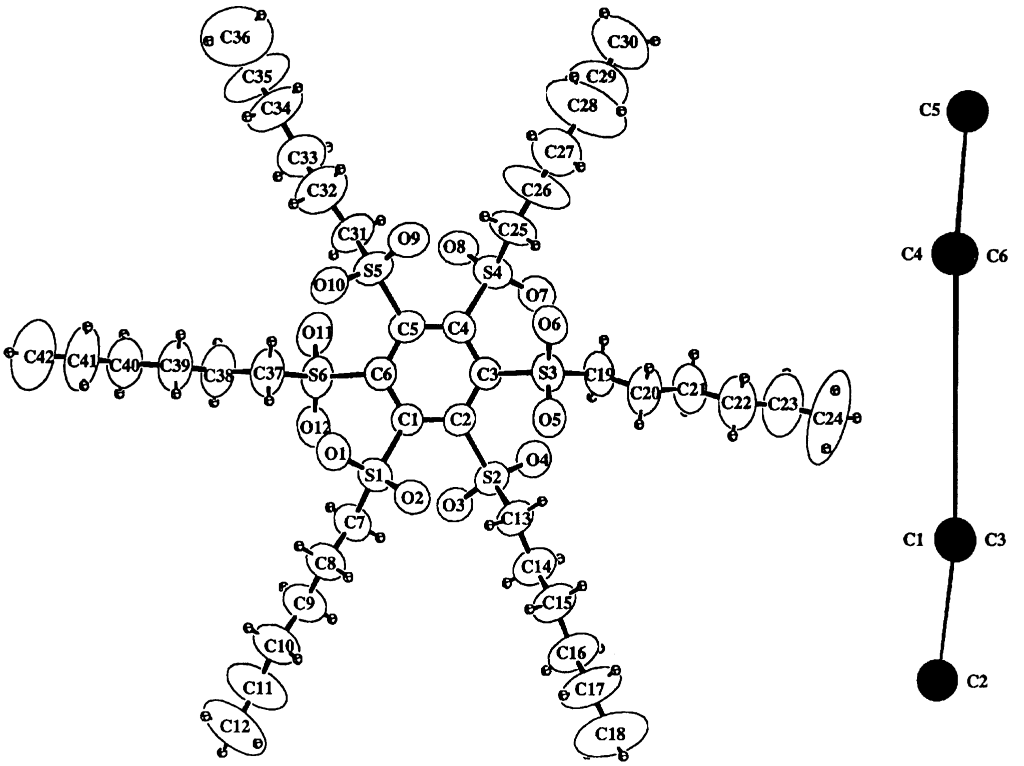


Fig. 1 Representative structure of **1e** determined by X-ray crystallography

four of the aromatic carbons (C1, C3, C4, C6) are nearly coplanar, while C2 and C5 are located above and below the C1—C3—C4—C6 plane by +0.089 and −0.055 Å, respectively. Consequently, the benzene ring is slightly deformed into a chair form with an average torsion angle of 6.75° for C_{ar}—C_{ar}—C_{ar}—C_{ar}; the folding angle with respect to the C1—C2—C3 C1—C3—C4—C6 plane is 5.84° (average). The torsion angle S—C_{ar}—C_{ar}—S is 44.65° (average). Bond lengths for C_{ar}—C_{ar} (1.406 Å) and S—C_{ar} (1.833 Å) are slightly longer than normal values, 1.390 Å and 1.764 Å, respectively.

Cyclic voltammetry characterisation of hexa(alkylsulfonyl)benzenes

Some members (**1a-f**) of the polysulfone **1** series exhibit rather unusual voltammograms in which the reduction and associated oxidation peaks are excessively separated.

Fig. 2 shows (exemplifying the case of the sulfone **1d**) a typical cyclic voltammetric behaviour at a polished platinum electrode (the shift in potential at very positive values prevented the use of mercury as a working electrode). Thus, the first peak located at E^1_{red} was found to be monoelectronic and totally irreversible at 25 °C for the investigated scan rate range between 0.02 and 10 V s^{-1}. The peak separation, ΔE, is 510 mV and is much larger than the theoretical value of 57 mV for a reversible behaviour at room temperature. In the case of **1a** (R = Me) the potential difference between the cathodic and anodic peaks was found to be ΔE = 480 mV and it may significantly increase with the size (and the bulkiness) of R. Complete voltammetric data for compounds **1a**–**f** in DMF are listed in Table 1.

When a thin layer voltammetric device was used[15], the global electrochemical process could correspond to a so-called quasi-reversible one-electron step (as clearly depicted in Fig. 3). The shape of the curve did not change at all upon repetitive cycling and peak integration revealed that one-electron steps were involved. Thus, multiscan CVs did not show loss of any of the starting material. From the linear sweep voltammetry data, the variation of peak potential E^1_{red} upon scan rate v between 0.02 and 10 V s^{-1} exhibited a slope of about 40 mV per decade of v, which is in close agreement[16] with an EC system, for which mixed kinetic control by the charge transfer and the following chemical reaction was reached.

When the switching potential was more negative than E^1_{red}, another irreversible cathodic peak located at E^3_{red} became visible. In addition, within the positive potential range explored, two irreversible peaks at E^2_{ox} and E^3_{ox} were seen (Fig. 2) together with a net decay of the first anodic step. The more anodic peak was confirmed to correspond to the oxidation of alkylsulfinate ions at a platinum electrode, formed by cathodic mono C—S cleavage of the corresponding sulfone.

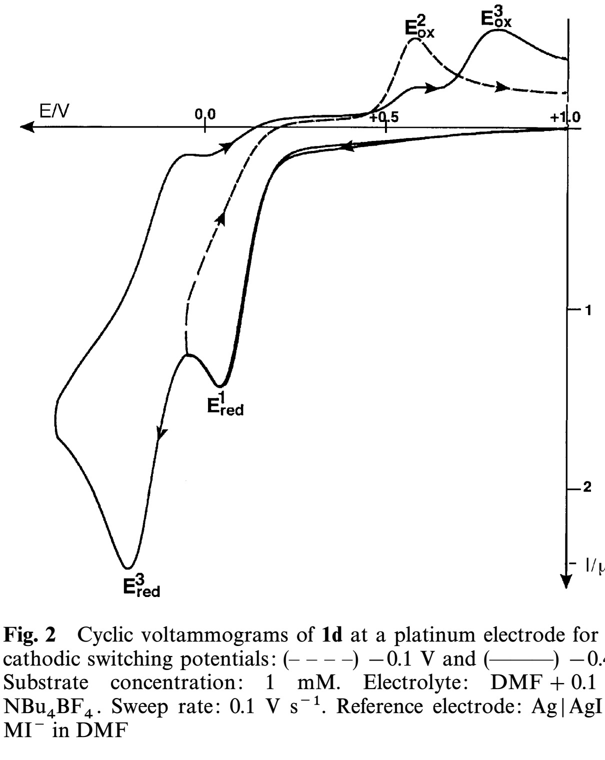


Fig. 2 Cyclic voltammograms of **1d** at a platinum electrode for two cathodic switching potentials: (– – – –) −0.1 V and (———) −0.4 V. Substrate concentration: 1 mM. Electrolyte: DMF + 0.1 M NBu_4BF_4. Sweep rate: 0.1 V s^{-1}. Reference electrode: Ag|AgI|0.1 MI^- in DMF

Table 1 Voltammetric data of hexasulfones at a polished platinum electrode[a]

Substrate	E^1_{red}/V	E^1_{ox}/V	E^2_{red}/V	E^2_{ox}/V	ΔE^b/mV
1a	0.17	—	—	0.65	480
1b	0.15	—	—	0.64	490
1c	0.08	—	—	0.59	510
1d	0.08	—	—	0.59	510
1e	0.02	—	—	0.68	660
1f	0.06	—	—	0.68	620
1g	0.30	—	0.54	0.65	350
1h	0.37	0.28	—	—	—
1i	0.03	0.10	—	—	—

[a] Hexasulfone concentration = 1 mM. Electrolyte: DMF + 0.1 M NBu_4BF_4. Sweep rate: 0.1 V s^{-1}. $T = 25$ °C. Reference electrode: Ag | AgI | 0.1 MI^- in DMF. [b] $\Delta E = E^2_{ox} - E^1_{red}$.

The shape of the cyclic voltammogram dramatically changed when the temperature was lowered ($T = -40$ °C). For example, with hexa(methylsulfonyl)benzene **1a**, the cathodic step became quasi-reversible ($\Delta E = 80$ mV) and the anodic peak at E^2_{ox} no longer appears (Fig. 4). Since a fast but reversible coupling of the radical anion appears to be excluded (slow k_D for tetra- and penta-sulfones, very weak dimerization : cleavage ratio with series **1** as demonstrated below), all this seems consistent with the conclusion that the two forms of the radical anion may co-exist: one stable at low temperature (**1A**$^{\cdot -}$ form) and the other at room temperature (**1B**$^{\cdot -}$ form).

As demonstrated previously by X-ray analysis, the molecular structure does show an undeniable distortion of the benzene ring, which suggests that polysulfone **1** would exist in the bulk in the chair form **A** at room temperature, while the radical anion could induce another parent structure we call **B**. The electrochemical reduction involves electron transfer to **1A**, forming an intermediate **1A**$^{\cdot -}$ that rapidly converts, at room temperature, into a stabilized **1B**$^{\cdot -}$ form. In contrast, at lower temperature it can be proposed that conversion of **1A**$^{\cdot -}$ into **1B**$^{\cdot -}$ could be frozen and therefore **1A** would show a fully reversible system.

Moreover, by changing structure parameters such as the length or bulkiness of the R groups, as well as the temperature and the accessible voltammetric sweep rate, a square diagram taking into account the equilibrium of the redox systems can be proposed (Scheme 1). For example, with R = ethyl, it was found that in the course of the second sweep at low temperature, both of the two steps turned out to be reversible if $v \geqslant 20$ V s^{-1} (Fig. 5). Voltammetric data at 276 K demonstrate then that the rate constant corresponding to the chemical transformation of **1A**$^{\cdot -}$ is $k_{A^{\cdot -}/B^{\cdot -}} = 220$ s^{-1}. The relevant activation energy is about 4.4 kcal mol^{-1}.

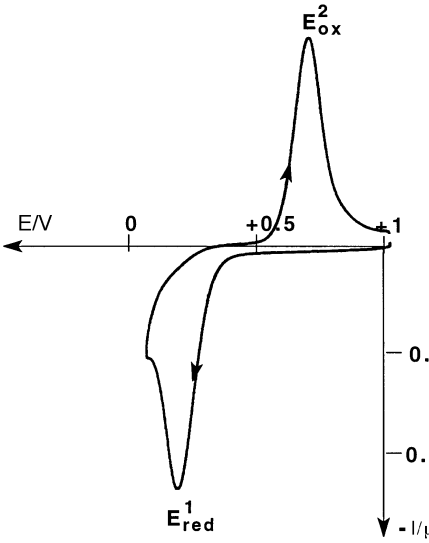


Fig. 3 Thin layer cyclic voltammogram of **1d** (concentration: 0.5 mM) at a fixed polished platinum electrode. Sweep rate: 0.05 V s^{-1}. Other conditions as in Fig. 2

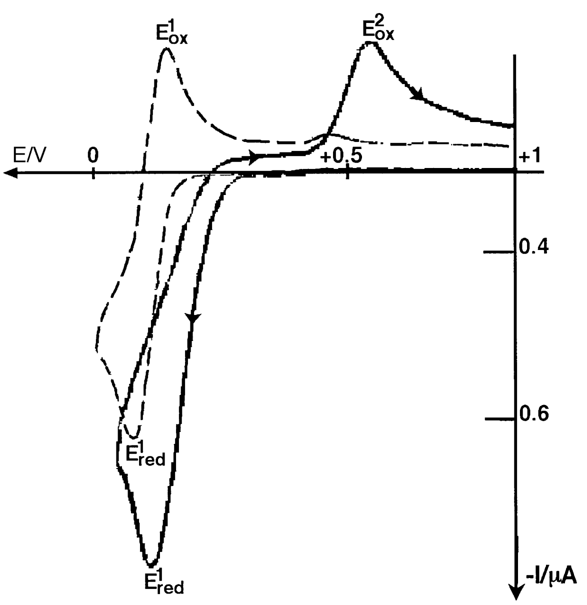


Fig. 4 Cyclic voltammograms at a platinum electrode of **1a** (concentration: 1 mM) at (———) 25 °C and (– – – –) −40 °C. Other conditions as in Fig. 2

$$\begin{tikzcd}
A + e^- \arrow[r, shift left, "k_{S,A}"] \arrow[d, shift left] & A^{\cdot -}\ (E^{0\prime}_A) \arrow[l, shift left] \arrow[d, shift left, "k_{A^{\cdot -}/B^{\cdot -}}"] \\
B + e^- \arrow[r, shift left, "k_{S,B}"] \arrow[u, shift left, "k_{B/A}"] & B^{\cdot -}\ (E^{0\prime}_B) \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

•For **1b**: $E^{0\prime}_A = 0.115$ V, $E^{0\prime}_B = 0.669$ V *vs.* Ag|AgI|0.1 M I^- at 276 K.

Scheme 1

Additionally, evidence for the existence of two neutral forms from **1** is provided by cyclic voltammetry of the most bulky sulfone **1g** (R = *iso*-propyl). As illustrated in Fig. 6(B), both of the two redox steps appear during the *first* sweep and the ratio of the corresponding current intensities varies with temperature and/or scan rate [Fig. 6(A)]. The first step would be predominant at room temperature while the second one is the lone reversible step at low temperature.

The conformational equilibrium is also shown by NMR spectroscopy at different temperatures from 273 to 328 K. Thus, ^1H NMR spectra of **1g** in $CDCl_3$ at room temperature exhibit three couples of well-differentiated isopropyl groups that are non-equivalent, as expected for a deformation of the phenyl ring. Upon lowering the temperature from 223 down to 173 K, no significant change in the resonance peaks was observed. In contrast, upon heating to 328 K the start of signal merging was observed. This result does confirm the fact that bulky hexasulfones are not planar and also could exist as an equilibrium mixture of a chair form (R neighbourhood of different groups is different) and a planar form (all R are equivalent).

On the contrary, most bulky hexa(alkylsulfonyl)benzenes with the isobutyl or benzyl moiety, such as **1h** and **1i** (Table 1), exhibited a lone reversible step (E^1_{red}) under all experimental conditions.

EPR spectra

Constant current electrolyses performed *in situ* in an EPR machine led to a rather stable paramagnetic signal with **1b**, **1d**

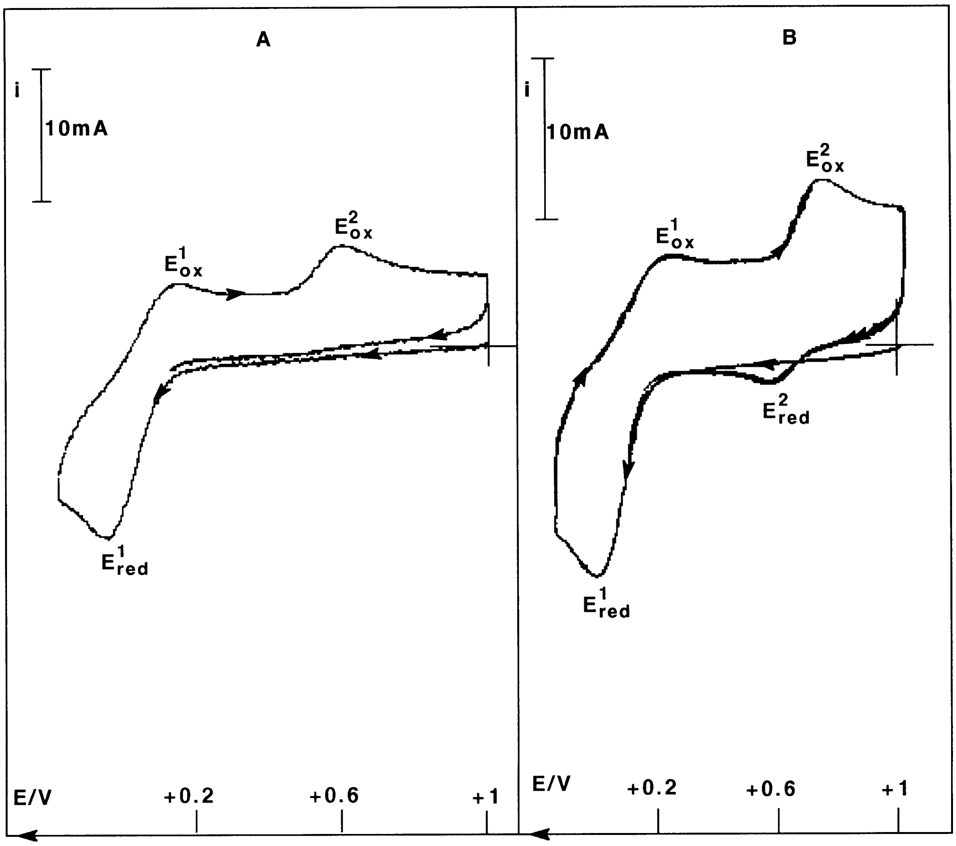


Fig. 5 Cyclic voltammograms at a platinum electrode of **1b** (concentration: 1 mM) at (A) 25 °C and (B) −20 °C. Sweep rate: 20 V s^{-1}. Other conditions as in Fig. 2

and **1f**. At room temperature, this signal rapidly became more complex with time, probably owing to the progressive formation of **2** by cleavage and the subsequent reduction into its stable radical anion $\mathbf{2}^{\cdot-}$. In contrast, at lower temperature ($T = -45$ °C) the signal (Fig. 7) remained quite stable and corresponded to a 1 : 2 : 1 triplet assignable to the radical anion $\mathbf{1}^{\cdot-}$ ($a_H = 1.66$ G: splitting with the CH_2 groups adjacent to the SO_2 moiety). Consequently, all the CH_2s at the

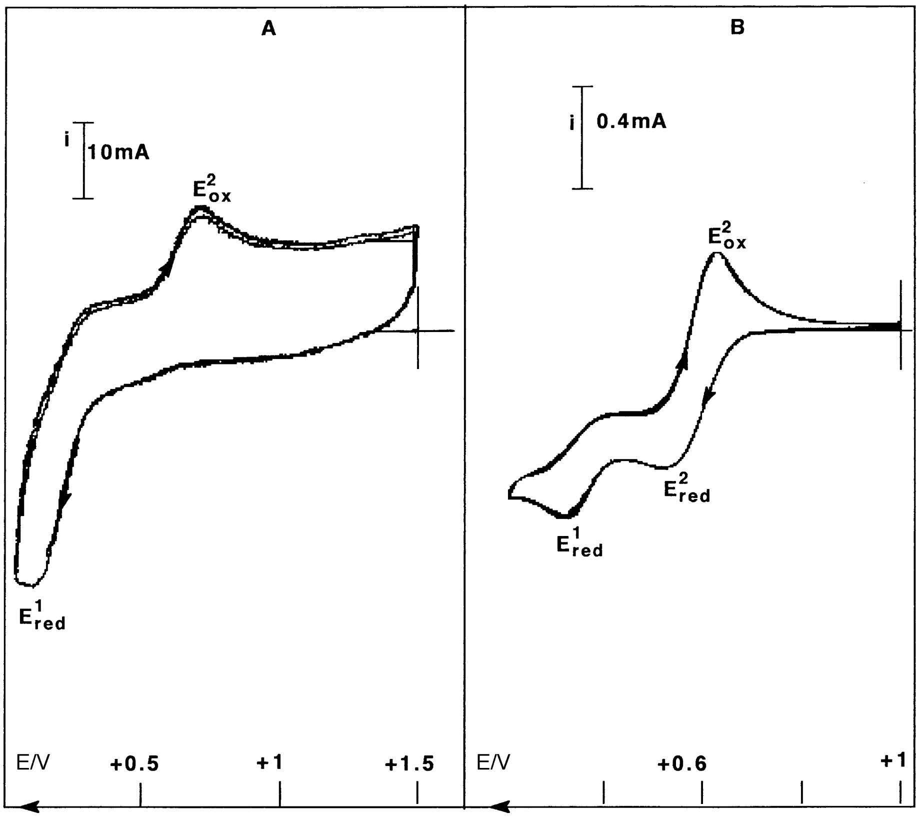


Fig. 6 Cyclic voltammograms at a platinum electrode of **1g** (concentration: 1 mM) at (A) 10 V s^{-1} and (B) 0.02 V s^{-1}. $T = 25$ °C. Other conditions as in Fig. 2

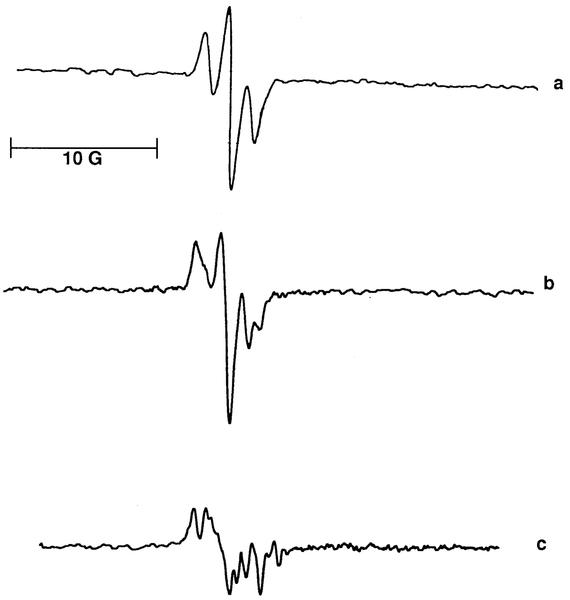
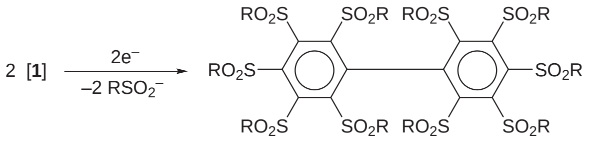


Fig. 7 EPR signals obtained in the course of a constant current *in situ* electrolysis of **1d** (R = butyl) in DMF + 0.1 M NBu_4BF_4. Fixed current: 20 mA cm^{-2}. Cathode: platinum grid (area: 1 cm^2). (a) Response at the beginning of the electrolysis at room temperature and at −45 °C (spectrum perfectly stable with time), (b) after 3 min and (c) after 6 min at room temperature

level of the radical anion would be equivalent, which would be consistent with a planar structure. Furthermore, the radical anion should possess a three-fold axis of symmetry if the six SO_2 groups were oriented alternately up and down as in neutral **1e**.

Macroelectrolysis experiments

Macroelectrolyses in DMF at the potential of the first peak (+0.08 V) led to two main reduction products, the penta(alkylsulfonyl)benzene and the dimeric form. From **1c**, **1d** and **1f**, penta(propylsulfonyl)benzene **2a**, penta(butylsulfonyl)benzene **2b** and penta(octylsulfonyl)benzene **2c** were obtained, respectively. Besides the cleavage products, the dimeric form **7** was also isolated from **1c**, **1d** and **1f** (after chromatographic separation from silica gel with diethyl ether as eluent).



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In DMF, electrolyses principally led to pentasulfones **2** (isolated yield: 15–20%). The substrate concentrations remained low (2 × 10^{-3} M, amount of substance: 5 mmol) owing to their very weak solubility. Under these conditions, the dimer yield was found to be quite low (about 1%).

In contrast, in methylene chloride the substrate solubility was much higher and the electrolyses carried out with **1d** (concentration: 8 × 10^{-3} M) afforded 20% dimer **7a** and 15% pentasulfone **2b** (isolated yields).

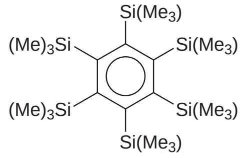
Discussion

It appears clear that electron transfer to very bulky aromatic structures like hexasulfonyl benzenes may induce, at least in certain cases depending on the experimental parameters (sweep rate, temperature), reorganization and structural changes. Thus, with relatively hindered hexasulfonylbenzenes (possessing essentially primary methyl to *n*-octyl R groups), it was established that one-electron steps obviously were involved with each of these structures, followed by a one-electron reoxidation process with a huge peak separation, often of the order of 0.5 to 0.7 V.

One can find throughout the recent literature pertinent examples of structural reorganization by means of cathodic electron transfer. But available examples do not describe any structural changes specifically relative to the aromatic ring. On the contrary, changes of structure (radical anion and dianion) were especially shown for many unsaturated flexible systems such as 1,3,5,7-cyclooctatetraene (COT), which exists in a so-called tub conformation in the neutral form, becoming an almost planar configuration with charge transfer.[19] Another example[20] that parallels experimental data already reported for COT concerns 3,8-dimethyl-2-methoxyazocine, for which the electron transfer was also accompanied by a ring flattening. Similarly, significant inner reorganizations were reported for the two-electron oxidation of 1,4-bis(dialkylamino)-1,3-butadiene[21] and for the two-electron reduction of some cycloalkane-1,2-diones.[22] Conformational changes were also reported[23] for radical anion(s) issued from bianthrone(s) and this example contrasts somewhat to the others given above since two well-established forms of the neutral substrate do exist in equilibrium. For bianthrone, the interconversion between these two thermochromic substances may be achieved through single electron transfer,[24] that is by anodic oxidation of the dianion into the relevant radical anion. More precisely, the two-electron transfer to the yellow-coloured form, which predominates at room temperature, leads to the green-coloured dianion involved at higher temperatures. The case of the lucigenin-10,10′-dimethyl-9,9′-biacrydylidene redox system was also reported.[25]

Consequently, the change of structure that is described here appears original for at least two reasons. Firstly, this event concerns the flat conformation of the central phenyl ring and requires only one reversible electron exchange. Moreover, the heterogeneous charge transfer rate constants k_s relative to the redox systems $\mathbf{A}/\mathbf{A}^{\bullet -}$ and $\mathbf{B}/\mathbf{B}^{\bullet -}$ were found to be rather large (greater than 10^{-2} cm s^{-1}).

The possibility for very bulky hexasubstituted benzenes to exist under two distorted forms was reported recently for hexakis(trimethylsilyl)benzene[26] **8** and 1,3,5-tris(dialkylamino)-2,4,6-trinitrobenzene[27] **9**.



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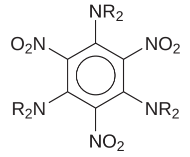

9

8 was reported to exist under two conformers: one D_3 ground state isomer possessing a boat form and the other having a higher energy with S_6 symmetry. The free energy difference given between the two conformers is 4.7 kcal† mol^{-1}.[26] Rather similarly, the structure of **9** (R = Et) was reported[27] to present two isomers of boat C_s and twist C_2 symmetry, seen to interconvert rapidly by means of a pseudo-rotation pathway. In this case, the interconversion barrier was found to be larger (9.1 kcal mol^{-1}). Such efficient π acceptors (**9**, R = H, Me, Et) were found[28] to exhibit very similar behaviour to the one reported here for hexasulfones **1**.

In light of the conformational evidence relative to these distorted benzenes, it can be proposed that compounds **1** do exist in the ground state as the chair conformer **A** while electron transfer, provided the structure is not totally frozen by a super hindrance of the substituents, will lead to a planar structure

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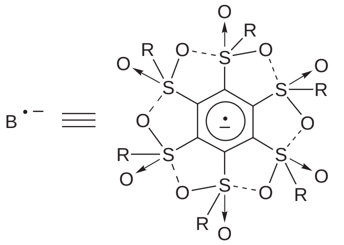
† 1 cal ≈ 4.2 J.

apparently favored, at the stage of the radical anion $\mathbf{B}^{\bullet -}$, by a donor-acceptor-like complex between the sulfur atoms and six of the oxygen atoms. This change in structure implies necessarily a rotation of $\pi/2$ radian around all the C—S aromatic bonds, bringing all these atoms in the plane of the phenyl ring.



It is expected that cooling down the electrolysis solution will freeze, at least for a short time, the highly unstable **B** structure after the reoxidation process. Thus, with R = Et, the barrier activation energy was calculated to be equal to 4.4 kcal mol^{-1}, while the difference in the free energy differences between the two rotamers, $\Delta\Delta G^\circ$, could be estimated at ≈ 12.7 kcal mol^{-1} from ΔE°. This relatively large value of $\Delta\Delta G^\circ$ could be explained by the large differences in structure between the assumed planar and chair conformations.

Further cyclic voltammetry experiments are currently in progress to evaluate the kinetic and thermodynamic parameters relative to the other hexa(alkylsulfonyl)benzenes. Also, it is aimed to extend the present study to parent polysulfoxides and polysulfonamides in order to find other examples of distortion for highly hindered benzene rings.

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