ELECTRON TRANSFER-INDUCED CONFORMATIONAL CHANGES OF HIGHLY HINDERED AROMATIC COMPOUNDS. CASE OF HEXAKIS(ALKYLSULFONYL)BENZENES

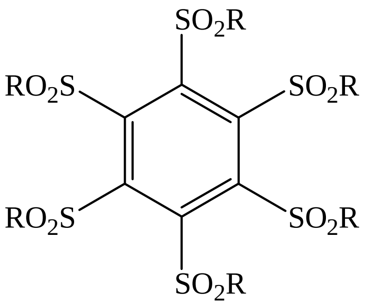
Bruno Fabre, Philippe Hapiot and Jacques Simonet

Laboratoire d'Electrochimie Moléculaire et
Macromoléculaire (Synthèse et Electrosynthèse
Organique - Unité Mixte de Recherche n°6510 associée
au CNRS), Université de Rennes 1, Campus de Beaulieu,
35042 Rennes Cedex, France

The monoelectronic reduction of hexakis(alkylsulfonyl)benzenes (alkyl = methyl **1a**, ethyl **1b**, butyl **1c**, *iso*-propyl **1d** and *iso*-butyl **1e**) to the corresponding radical anion in dimethylformamide involves two largely separated redox systems, except in the case of **1e** that shows a single perfectly reversible system. This unusual behavior can be explained by the existence of two conformers that are easily interconverted through single electron-transfer.[1,2]

If conformational changes have been reported in several instances in electrochemical investigation, they are generally associated with multi-electronic reduction. In that sense, the reduction of these substituted sulfones that are chemically reversible and involve only one-electron reduction appears to be special. Electrochemical data supported by calculations of molecular modeling (DFT and PM3 methods) show the existence of a four-member square scheme for which the neutral and radical anion species can both exist under chair and boat conformations (Scheme 1).

An essential feature of this study is the control of the structural changes of the benzene ring through the size and more particularly, the steric hindrance of the alkyl substituents. So, various situations can occur depending on both kinetics and thermodynamics of the conformational interconversion between the chair and boat forms. Linear alkyl chains-substituted derivatives (namely, **1a-c**) are stable under their chair forms whereas their respective radical anions adopt a boat-like geometry. The coexistence of the two conformers is observed at the neutral state for hexakis(*iso*-propylsulfonyl)benzene **1d** whereas the most hindered *iso*-butylsulfonyl-substituted compound **1e** is locked in a chair form. Such a conformational versatility within a same class of aromatic compounds is an interesting possibility for the design of molecules in which large conformational modification can be triggered by a single electron transfer. Through a fine-tuning of the length and the steric hindrance of the alkyl group, it seems possible to control the relative stabilities of the different redox species.



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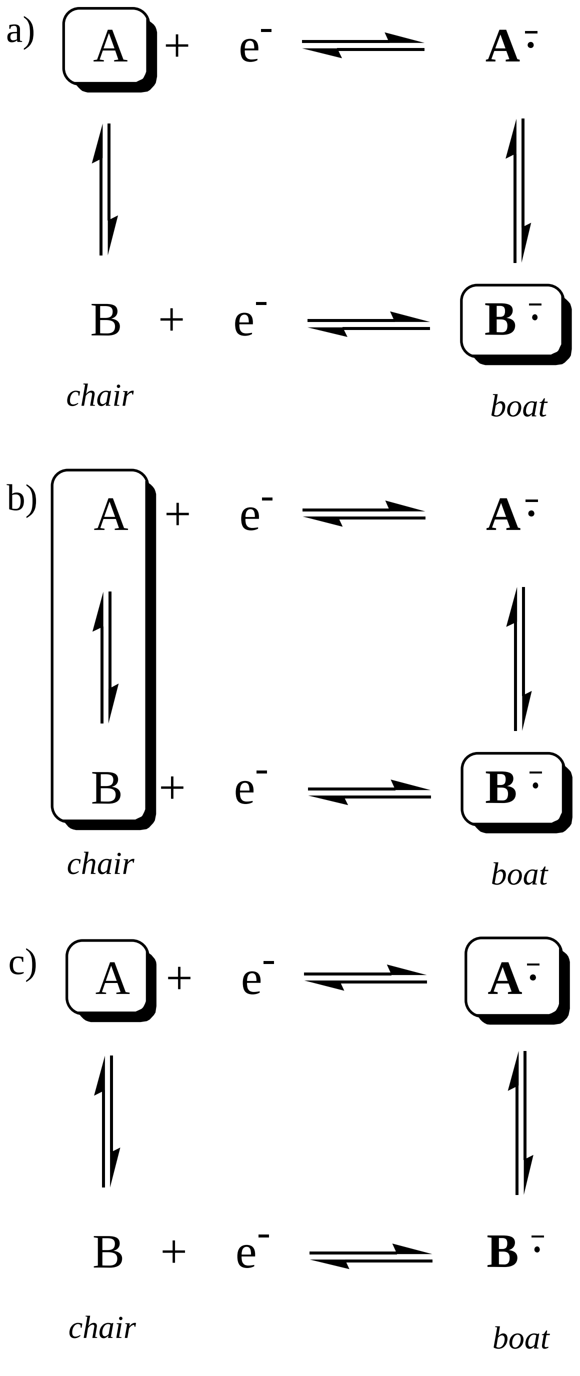
R =	
1a	Methyl
1b	Ethyl
1c	Butyl
1d	*Iso*-propyl
1e	*Iso*-butyl



Scheme 1. Square schemes depicting the most stable redox conformers as a function of the alkyl substituent. (a) ***1a****,* ***1b*** *and* ***1c****, (b)* ***1d****, and (c)* ***1e****.*

(1) Fabre, B.; Hapiot, P.; Simonet, J. *J. Phys. Chem. A* **2002**, *106*, 5422.
(2) Ghanimi, A.; Fabre, B.; Simonet, J. *New J. Chem.* **1998**, 831.