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Volume 28

Edited by

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Preface

In pursuit of the objective of the series, which is to present considered reviews of areas concerned with the quantitative study of organic compounds and their behaviour – physical organic chemistry in its broadest sense – in a manner accessible to a general readership, this twenty eighth volume contains five contributions on a diversity of topics. Two of these reflect the increasing importance of physical organic studies in providing fundamental knowledge relevant to the development of new materials with novel physical properties. The others represent more traditional areas of physical organic interest, where recent research has thrown new light.

As ever, the Editor and his Advisory Board invite comments, criticism (preferably, but not necessarily, constructive) and proposals from readers and potential writers. Suggestions concerning developments in physical organic chemistry where a forward-looking review might help in the development of a new research area, or of established topics in need of an up to date treatment, should be directed to any of us.

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Electron Storage and Transfer in Organic Redox Systems with Multiple Electrophores

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1 Introduction

Unsaturated carbo- and hetero-cycles are known to constitute active electrophores that can be subjected to chemical or electrochemical redox processes forming persistent cations or anions. Depending on the number of electrons transferred, the charged products can be either diamagnetic or paramagnetic. Crucial questions in describing the redox-activity of cyclic π -systems concern: (i) the number of accessible redox-states (Meerholz and Heinze, 1989, 1990); (ii) the mode of charge distribution (Heilbronner and Bock, 1978; Salem, 1966; Eliasson *et al.*, 1986, 1990); (iii) the stabilization of charge by ion-pairing and/or conjugative effects (Hogen-Esch, 1977; Müllen *et al.*, 1990); (iv) the possibility of charge-induced configurational and conformational changes (Eliasson *et al.*, 1986; Huber and Müllen, 1986); (v) the chemical reactivity (Hogen-Esch, 1977; Szwarc, 1968; Müllen, 1986,

1987). A particularly attractive group of substrates are the annulenes, since electron transfer allows an interconversion of $(4n + 2)\pi$ - and $(4n)\pi$ -systems, and thus a switch between π -bond delocalization and π -bond localization (Müllen, 1984).

A relevant step from the viewpoint of electron-transfer activity is the linking of two or more identical electrophores to bis-, oligo- or polyelectrophoric systems. In an attempt to extrapolate the description of the single electrophore to that of the higher homologues, the above questions maintain their significance, but additional attractive aspects arise. First of all, it is appropriate to subdivide multi-electrophoric species into two classes depending on whether the linkage between the building blocks is an unsaturated or saturated chemical unit. In the former case, with extended π -conjugation, one expects successive electron-transfer steps to create strongly interacting redox states in which the excess charge is distributed over the whole π -system. In the latter case, with electronically "decoupled" electrophores, one expects the electron-transfer steps to occur independently, with only electrostatic interactions of the redox states; the excess charge is localized on the electrophores (Smith *et al.*, 1976; Flanagan *et al.*, 1978). Within the domain of materials science, the classification of multi-electrophoric organic systems according to the mode of linking of the subunits has led to the definitions of conducting polymers and redox polymers (Wegener, 1981; Baughman *et al.*, 1982; Heinze, 1990; Nowak *et al.*, 1980; Murray, 1984).

The present review is restricted to "dimeric" or (low molecular weight) "oligomeric" redox systems with identical, electronically decoupled electrophores A. Consider the biselectrophore A–I–A, where I represents a saturated spacer (Fig. 1A). Injection of an electron into one subunit A under formation of a radical anion raises the immediate question of whether the electron will tend to localize in the original subunit or whether it will undergo a degenerate electron transfer to the neighbouring unit. In the terminology of electron-transfer kinetics such electron hopping between identical redox groups is termed self-exchange (Cannon, 1980). Depending upon the rate of this process, one will observe an "effective delocalization" over two or more units within the timescale of the experiment, or a localization of charge on one unit.

Upon further contact with a redox reagent or at higher redox potentials, additional electrons can be transferred. After a two-electron transfer, each redox unit can accept one charge with formation of a singlet or triplet dianion, or (less favourably from an electrostatic point of view) both charges can enter one redox unit. Here again, an intramolecular electron-exchange process is possible.

Further relevant questions concern the nature of the highest accessible

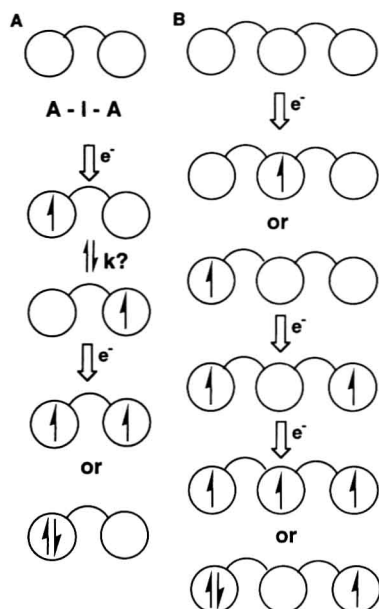


Fig. 1 Charging of a biselectrophore (A) and a triselectrophore (B).

redox state and the way in which the molecule copes with the increasing electrostatic repulsion. Clearly, the charging mechanism of the substrate and the particular electron-transfer kinetics are expected to be more complicated if the redox groups are different; this can be the case in the homologous tris-electrophore (Fig. 1B), since the outer and inner electrophoric units now have a different substitution pattern, or in the bis-electrophore A-I-A when one unit A is slightly perturbed, e.g. by alkyl substitution.

A major concern of this review is the tailoring of the redox behaviour of organic compounds, i.e. the optimization of such systems for electron storage and electron hopping. While the emphasis is on reduction and thus on anion formation, it has been shown on many occasions that oxidative cation formation leads to analogous conclusions (Meerholz and Heinze, 1990; Lewis and Singer, 1965). The structure of this text is thus obvious.

- (a) One will first have to consider the design and synthesis of suitable systems in which the structural conditions relevant for the energy profiles of inter- and intra-molecular electron-transfer processes can be systematically varied. The variation of the structure comprises the nature of the redox-unit A and of the spacer I. It will be shown that

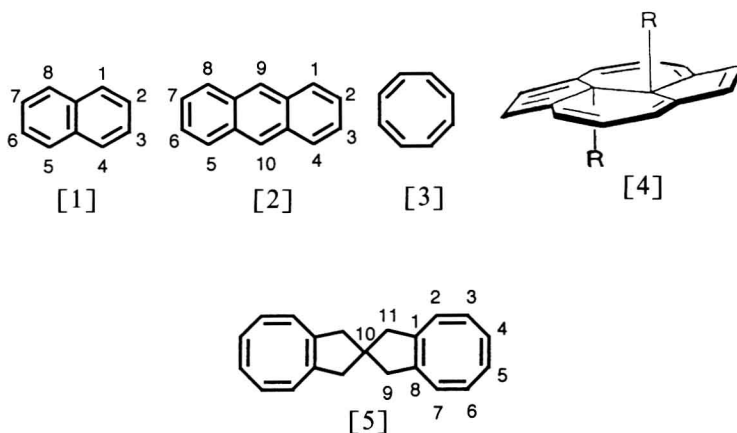
this can be brought about readily by the synthetic technique of reductive alkylation (Müllen, 1984, 1986, 1987).

- (b) The second question is whether such species can serve as efficient electron acceptors in successive charging reactions. This aspect, if expressed in terms of structure, will focus on electrophores A that can be charged to a high charge density and on spacer groups I that tend to minimize the consequent Coulombic repulsion. It is obvious that this approach is closely related to the search for organic electron-storage materials that can be used as battery electrodes (McDiarmid, 1979; Bitthin *et al.*, 1987; Shacklette *et al.*, 1987).
- (c) A third question concerns the sequence of the successive charging processes. It is clear that, depending on the particular charging mechanism and upon the number of electrons transferred, one can arrive at para- or dia-magnetic products that differ in the prevailing charge (spin) density distribution.
- (d) The fourth and main topic is how the *intramolecular* electron transfer between the redox groups of the systems depends upon structural phenomena. The energy profiles of intramolecular electron-transfer processes are important for many areas of chemistry. Some representative examples are (i) the photochemically induced electron transfer and the lifetime of charge-separated states in porphyrin-quinone diads, which serve as model compounds in photosynthetic studies (Gust *et al.*, 1986, 1988; Wasielewski *et al.*, 1985); (ii) the possibility of a long-range electron transfer and the relation between rate and reaction enthalpy according to the Marcus theory (Marcus, 1956, 1963, 1965) in benzenoid species attached to a steroidal spacer (Closs and Miller, 1988; Closs *et al.*, 1989; Liang *et al.*, 1990); and (iii) the influence of chain length and chain conformation on electron transfer between metal complexes (Reimers and Hush, 1990; Gray and Malmström, 1989), e.g. at the ends of an oligopeptide chain (Isied *et al.*, 1988).

In contrast with these approaches, the present account is restricted to *degenerate*, intramolecular electron transfer occurring in the charged *ground state* of the bis-electrophore A-I-A. It should be emphasized that our approach is a purely empirical one: knowledge of the structural dependence of the charge-storage capacity and of intramolecular electron-hopping processes might enable us specifically to design dimers, oligomers and polymers in which the electron-transfer rate, and thus the resulting charge distribution, can be controlled precisely.

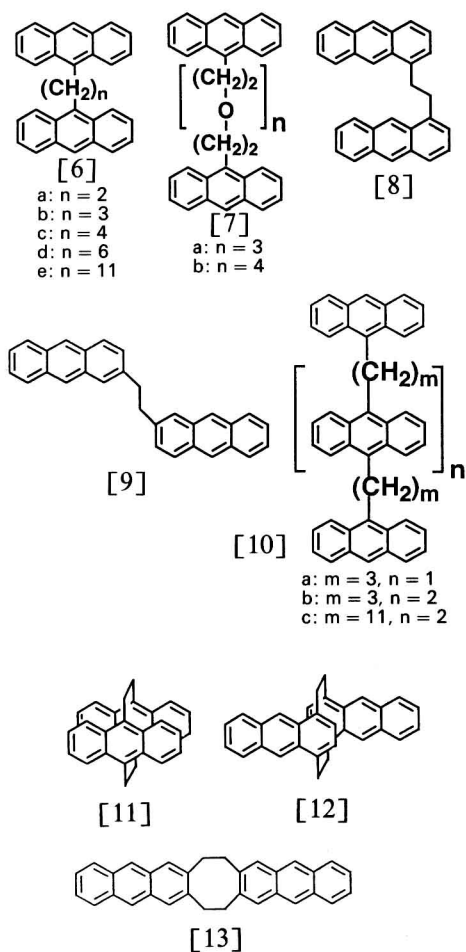
2 Design and synthesis

It is appropriate to begin with an overview of the compounds that have been specifically selected and synthesized for the present purposes. They are made up of redox-active subunits such as the benzenoid hydrocarbons naphthalene [1] and anthracene [2], the $[4n]$ annulene cyclo-octatetraene [3] and the bridged (aromatic $= 4n + 2$) $[14]$ annulene [4]. Each subunit is known to form a radical anion and dianion in chemical or electrochemical reductions (Meerholz and Heinze, 1989; Rabinovitz, 1988). Cyclo-octatetraene is an outstanding electrophore because, in the course of an electron transfer, its tub-shaped structure undergoes a flattening of the ring, while the other hydrocarbons possess rigid π -systems that do not experience extensive structural change upon undergoing a redox process (Katz, 1960; Anet *et al.*, 1964; Heinze *et al.*, 1974).



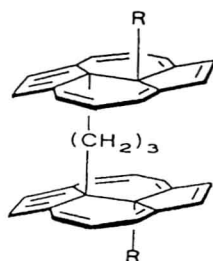
When linking these redox-active building blocks to form dimers and oligomers, care has to be taken to vary the steric and electronic interaction of the subunits systematically. In [5] an orthogonal arrangement of the two of the subunits systematically. In [5] an orthogonal arrangement of the two cyclo-octatetraene units is enforced (via the spiroconjugation). Compounds [6]–[10] contain a flexible connection of the anthracene species, while in the arrangement.

Another type of face-to-face-arrangement is found in the multi-layered annulene systems [14] and [15]. Here, unlike the para-cyclophanes, in which the phenyl units are connected by “external” alkanediyl groups, the stacking of annulene layers is achieved by “internal” linkages, with the bridge located inside the π -clouds. The advantage of the latter structure is that one can

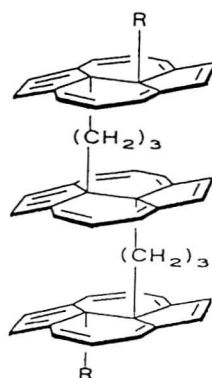


readily vary the inter-plane distance and that the multi-layered system can be created in a true polymer forming reaction (see below).

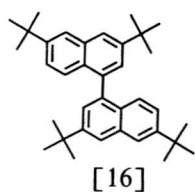
The common feature of compounds [5]–[15] is that the electrophoric units are linked by saturated spacers, thus establishing only weak electronic (through-bond or through-space) interaction of the π -systems. In contrast, the binaphthyl [16], the biperylenyl [17] and the bianthryl [18] as well as the structurally related homologues [19], [20] and [21] allow for a direct π,π -interaction of the subunits; it will be shown, however, that for both steric and electronic reasons the inter-ring conjugation can be weak and thus lead to electronically independent redox groups in a similar fashion as in [5]–[15].



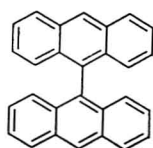
[14]a: R = CH₃
b: R = 2-dodecyl



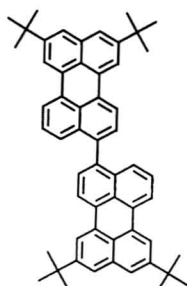
[15]a: R = CH₃
b: R = 2-dodecyl



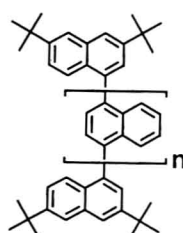
[16]



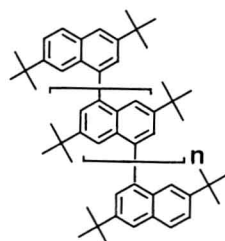
[18]



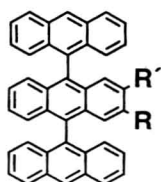
[17]



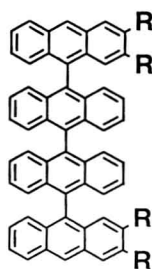
[19]



[20]

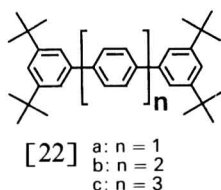


21a: R = R' = hexyl
21b: R = H, R' = isopentyl



21c: R = hexyl

[21]



Compounds [6] and [7] have been described in the literature (Müllen, 1987; Fiedler *et al.*, 1986; Huber *et al.*, 1983). The ortho-anthracenophane [13] has been prepared by Diels–Alder cycloaddition as part of a project devoted to ladder-type polymers (Wagner *et al.*, 1988; Wegener and Müllen, 1991; Pollmann *et al.*, 1990). Compound [17] as well as the oligomers and polymers [19]–[22] have been prepared recently using various methods of aryl–aryl coupling (Bohnen *et al.*, 1990; Fahrenstich *et al.*, 1989; Koch and Müllen, 1991; Baumgarten *et al.*, 1992a; Schenk, 1989). The most appropriate method, however, for the versatile linking of conjugated hydrocarbons by saturated spacer groups is reductive alkylation (Müllen, 1984, 1986, 1987; Bender *et al.*, 1988, 1989; Bender and Müllen, 1988; Krummel and Müllen, 1988). This approach is based on the formation of carbanionic hydrocarbons by reduction of conjugated π -systems or by deprotonation of dihydro-precursors and their subsequent reaction with electrophilic reagents such as haloalkanes in S_N2 -type reactions.

For the synthesis of the bis-cyclo-octatetraene compound [5] (Krummel *et al.*, 1987; Auchter-Krummel and Müllen, 1991), cyclo-octatetraene dianion was quenched with tetrabromoneopentane to give the bis-adduct [23], which exists in an equilibrium between valence isomers [23a] and [23b]. Hexacycle [23a] was actually isolated in about 60% yield (Fig. 2) (Krummel *et al.*, 1987). Accordingly, in the subsequent dehydrogenation, the formation of [23a] must be avoided by working at low temperatures; in this case it was possible to deprotonate the originally formed isomer [23b], obtaining a

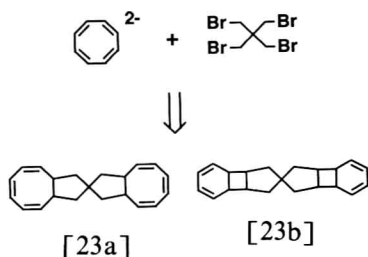


Fig. 2 Quenching of cyclo-octatetraene with tetrabromoneopentane.