THE DIFFERENT REDOX-ACTIVITY OF DIANTHRYLBENZENE AND DIANTHRYLBIPHENYL

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Abstract: The reduction of dianthrylbenzene and dianthrylbiphenyl to stable
tetraanion salts is described by NMR spectroscopy and cyclic voltammetry. The
significantly different Coulomb interactions between the anthracene units are
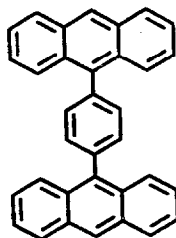compared with those in dianthrylalkanes.

We have recently shown that successive one-electron reduction of dianthrylal-
kanes 1 generates a complete redox sequence ranging from a radical monoanion
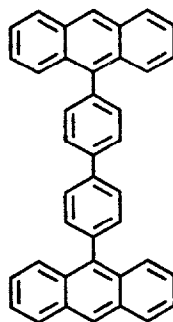up to a tetraanion.[1] Having characterized 1 as efficient electron storage
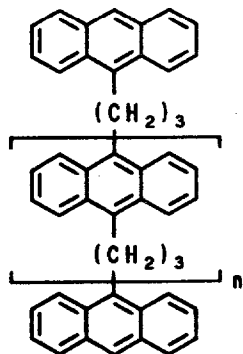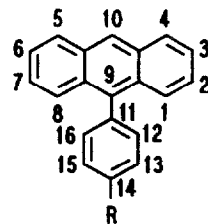

1 n = 0

2 n = 1

3 n > 10

4

5

6 R = H

7 R = CH_3

systems we synthesized the corresponding trianthryl species 2[2] and the related
polymer 3.[3] Cyclovoltammetric and chemical evidence indicated that each an-
thracene subunit of 2 and 3 can be charged with two electrons.

The characteristic electrochemical differences observed between conducting and redox polymers[4,5] strongly suggested that the comparison of 1 - 3 with analogous compounds, in which anthracene redox centers are linked by unsaturated instead of saturated bridges, would be of interest. Typical examples of unsaturated linkages are provided by the incorporation of benzene or biphenyl units as in compounds 4[6] and 5. These hydrocarbons can, in principle, establish an extended π-conjugation so that the anthracene units do not act as independent redox centers.

The previously unknown 4,4'-bis(9''-anthryl)biphenyl (5) was synthesized by the reaction of 4,4'-dilithiobiphenyl (prepared from 4,4'-dibromobiphenyl and butyllithium) with anthrone and subsequent dehydration with HCl/ethanol.[8]

The chemical and electrochemical reduction of 4 and 5 was investigated. The anionic salts of the 9-arylanthracenes 6 and 7 were prepared as model systems. The crucial questions are (i) whether 4 and 5 are similarly effective charge acceptors as their saturated counterparts 1 and 2, (ii) what is the mode of charge distribution and (iii) what is the degree of Coulomb repulsion between the charged units.

Table 1: ^{1}H-NMR chemical shifts (δ_H) of 4-7 and their ionic derivatives[a]

	H-1,8	H-2,7	H-3,6	H-4,5	H-10	H-12,16	H-13,15	H-14	H-CH$_3$
4	7.93	7.49	7.49	8.12	8.62	7.69	7.69		
4^{4-}/4Li$^+$	3.44	4.12	4.25	3.60	1.82	6.52	6.52		
5	7.80	7.48	7.41	8.07	8.53	7.98	7.58		
5^{4-}/4Li$^+$	4.48	5.03	5.03	4.92	2.58	6.94	6.73		
6	7.70	7.61-7.33		8.06	8.51	7.61-7.33			
6^{2-}/2Li$^+$	4.87	5.17	5.33	5.59	2.86	7.24	6.42	7.07	
7	7.67	7.43	7.31	8.05	8.52	7.37	7.29		2.50
7^{2-}/2Li$^+$	3.88	4.42	4.59	4.42	2.09	6.88	6.52		2.00

a) [D$_8$]-tetrahydrofuran, 200 MHz, -30 °C; the signal assignments for the ion salts have been made from the splitting patterns and H,H-decoupling experiments.

The title compounds 4 - 7 were subjected to reduction with lithium in [D$_8$]-tetrahydrofuran (THF) at -30 °C under ^{1}H-NMR spectroscopic control. The deeply coloured diamagnetic products finally obtained were characterized by their well-resolved ^{1}H-NMR spectra. The spectra indicated that the molecular frameworks remained intact and also provided information on the number of charges adopted. The number of extra charges was also inferred from quenching experiments, i.e. from the number of methyl groups which, according to MS-analysis, were incorporated upon reaction of the polyanions with dimethyl sulfate. It appears that the dianthryl compounds 4 and 5 transform into tetraanion salts while 6 and 7[7] give rise to dianion salts. Their NMR chemical shifts are listed in Table 1.

Cyclic voltammetric experiments carried out in liquid dimethylamine with tetrabutylammonium bromide as supporting electrolyte show that $\underline{4}$ and $\underline{5}$ can be reversibly reduced in four one-electron steps to their respective tetraanions (Table 2). The formation of the monoanions occurs at $E^\circ_{R/R^{\pm}} \approx -1.92$ V vs. Ag/AgCl, a redox potential which is similar to that of the first reduction step observed in $\underline{1}$ and $\underline{2}$. For $\underline{4}$ and $\underline{5}$ both the height of the peak current, which is nearly twice the value of pure one-electron reduction waves, and the peak potential separation of approximately 45 mV (T = -65°C) between the cathodic and anodic wave[9] indicate that the redox potentials of the dianion formation are separated from the $R/R^{\pm}$ redox couples by only about 70 and 20 mV, respectively.

Table 2: Redox potentials of $\underline{4}$ and $\underline{5}$[a)]

R	$E^\circ_{R/R^{2-}}$ [b)]	$E^\circ_{R^{2-}/R^{3\pm}}$	$E^\circ_{R^{3\pm}/R^{4-}}$
$\underline{4}$	-1.99 (70)	-2.65	-2.80
$\underline{5}$	-1.90 (20)	-2.34	-2.67

a) Cyclic voltammetry at a Pt-electrode (ϕ = 1mm) with solution 10^{-4} M in substrate and 0.1 M TBABr for $(CH_3)_2NH$. All potentials in V vs.Ag/AgCl (calibration with $[Cp_2Co]^+/[Cp_2Co]$.) T = -65°C. Scan rate = 100 mV/s. b) "2e"-redox steps, in brackets ΔE° differences (in mV) between the $R/R^{\pm}$ and the $R^{\pm}/R^{2-}$ couples.

The further reduction of $\underline{4}$ to its stable trianion at $E^\circ_{R^{2-}/R^{3\pm}} = -2.65$ V is similar to the case of 1,3-dianthrylpropane $\underline{1}$. This potential, in agreement with expectations, is 650 mV more negative than the corresponding redox potentials for the dianion formation. The last reduction step of $\underline{4}$ to the tetraanion takes place at a further 140 mV more negative potential $E^\circ_{R^{3\pm}/R^{4-}} = -2.80$ V. In contrast, the generation of the tri- and tetraanions of $\underline{5}$ is already observed at redox potentials of -2.34 V ($\Delta E^\circ_{2,3}$ = 440 mV) and -2.67 V ($\Delta E^\circ_{3,4}$ = 330 V), respectively.

The NMR spectroscopic and cyclovoltammetric results provide a firm answer to the first question: the formation of highly charged species is possible in a way quite similar to compounds $\underline{1}$ and $\underline{2}$ with little interaction between the charged anthracene units.

The distribution of the excess charge between the anthracene and the bridging units could, in principle, be inferred from the charge-induced shielding effects (see Table 1). Complications arise from the fact that ion formation can also change the ring current effects and that the anisotropic influence of the latter depends on the relative orientation of anthracene and bridging unit. Dianion formation in anthracene itself is known to cause a shielding of the protons which is much more pronounced than is expected from the sole charge effect.[10] This strong shielding, which must be ascribed to some paratropism in the 16π-system, is also obvious for $\underline{6}^{2-}/2Li^+$ and $\underline{7}^{2-}/2Li^+$, i.e.

the relatively small portion of the excess charge residing on the phenyl or tolyl substituent does not significantly affect the ring current properties of the anthracene moiety. Obviously, a related finding holds for $4^{4-}/4Li^+$ and $5^{4-}/4Li^+$. However, upon going from the neutral to the charged species the shielding of anthracene protons is smaller in 5 than in 4, while the reverse order is observed from the "bridge" protons. Accordingly, the biphenyl bridge accepts a considerable amount of the excess charge.

It follows from the separation of the R/R^- and R^-/R^{2-} redox couples of 4 and 5 that the Coulomb repulsion between the anthracene groups is weak and virtually independent of the length of the unsaturated bridge. The interaction in the case of 4 is comparable to that in 1. This supports the assumption that the benzene bridge does not promote a conjugative interaction in the dianion of 4, but acts only as a spacer which allows the anthracene groups to interact purely electrostatically. In the case of 5 the electrostatic interaction is not even detectable in the dianion. The main portion of the excess charge in these redox-active π-systems is therefore localized in the anthracene units. The similarity of the charge effects in 4 and 1 strongly supports the view that the nature of the Coulomb interaction between the highly reduced anthracene dianion subunits of 4^{4-} is still electrostatic. By contrast, the facile formation of the trianion of 5 and the large spacing to the redox step of the tetraanion indicate that, in agreement with the NMR data, the biphenyl bridge is significantly charged, thus causing strong Coulomb repulsion in the tetraanion. Although at a first sight this effect seems difficult to grasp, a comparison of the redox potentials of biphenyl monoanion formation and anthracene dianion formation shows that their values – –2.68 V and –2.64 V[11] – are very similar. Therefore the conjugative coupling of these two redox-active sites should generate inter alia an energetically more favourable redox level.

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8. 9 % yield after recrystallisation from dichloromethane/ethyl acetate (m.p. > 300 °C). NMR spectroscopic data of 5 see Table 1, λ_{max} (CH_2Cl_2) 217 nm (lgε 4.77), 258 (5.42), 350 (4.21), 368 (4.40), 387 (4.40); MS (70 eV) m/z 506 (M^+, 0.1 %), 330 (0.6), 85 (24), 83 (35), 71 (11).
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