2-(2-Arylvinyl)-9,10-anthraquinones: Combined Electro- and Photo-chromic Properties for Molecular Switching

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Easily prepared and novel anthraquinone derivatives, containing photochemically isomerisable 4'-substituted stilbene functions, may be interconverted electrochemically between four states, each capable of existing as *cis*- or *trans*-isomers.

For organic compounds photochromism is well established as is electrochromism in the form of reversible electrochemical interconversion between colourless redox states (usually neutral starting materials) and coloured states (usually radical-ions or di-ions).

Substituted azobenzenes such as 1 and 2 have been shown[1,2] to exhibit interesting photoelectrochemical behaviour based on the reducibility of the –N=N– group combined with the possibility for *cis–trans*-photoisomerisation. These concepts have been taken further and recent reports[3,4] describe organic systems (3 and 4) which have functional groups capable, separately, of reversible photochemical and electrochemical change. Such systems may be important for inclusion in devices capable of repetitively storing, revealing, and re-revealing images or information in response to photochemical or electrochemical stimuli. The azobenzene systems are not highly stable, a disadvantage should long-term use be envisaged and the products of their reduction (hydrazobenzenes) give rise to highly toxic by-products. Furthermore, the azo function is relatively easily reduced [PhN=NPh, $E_{p,c}(1) = -1.36$ V *vs.* standard calomel electrode (SCE); *cf.* anthraquinone, $E_{p,c}(1) = -0.98$ V (*vs.* SCE), both measured in dimethylformamide (DMF)–Bu$_4$NClO$_4$ (0.1 mol dm^{-3})];[5] on the time-scale of steady-state experiments homogeneous electron transfer between the two electrophores, with a ΔE_p of 0.38 V, might be a complicating factor.

System 4 has been examined[4] in impressive detail; the reduction potential of the anthraquinone function is sufficiently lower (less cathodic) than that of the chromophore, in its cyclised form. On photochemical ring-opening the reduction potential is significantly lowered probably, by analogy[6] with other dicyanoethylene compounds, because of competing reduction of that group.
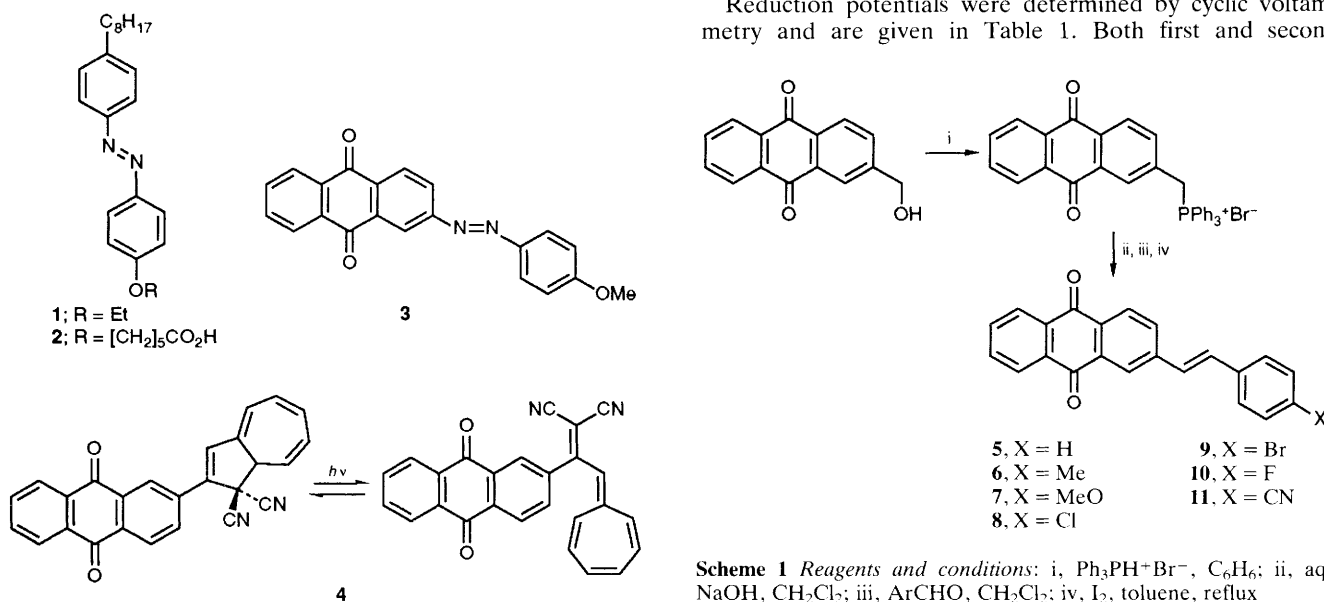
We are prompted by these recent reports to describe our experiments with 2-(2-arylvinyl)-9,10-anthraquinones, a series of novel compounds which are relatively easy to prepare, are considerably stable, and have functional groups which may separately and reversibly undergo redox reactions (with electrochromism) or photoisomerisation (with photochromism). They may also be prepared with a wide range of substituents in the photochromic moeity.

The compounds involved, 5–11, and the route used for their preparation, are given in Scheme 1. The quinone function undergoes, in aprotic solution, reversible reduction; the carbon–carbon double bond, by analogy with stilbene, undergoes reversible *trans–cis*-isomerisation under UV irradiation. In principle, the states given in Scheme 2 may be achieved and interconverted by control of the electrochemical and photochemical parameters. The starting materials are typically pale yellow–orange whereas both the one-electron and two-electron reduction products (radical-anions and dianions respectively) are deep red in aprotic solution. In the presence of proton donors the pale-green hydroquinones are formed; these are easily oxidised back to the quinones.

Compounds 5–11 were prepared as pure *trans*-isomers and their electrochemical and photochemical properties compared with those of mixtures of the *cis* and *trans*-isomers prepared by UV irradiation of solutions of the *trans*-isomer (Table 1). As anthrquinone can act[7] as a photosensitiser for the interconversion of *trans*- into *cis*-stilbene it is likely that in the compounds under study the anthraquinone moiety fulfils this function. The composition of the mixtures was determined by integration of the characteristic ^{1}H NMR absorptions of the vinylic protons, *e.g.* for *trans*-5, $\delta[(CD_3)_2CO] = 7.52, 7.65$ (*J* 16 Hz) and for *cis*-5, 6.85, 6.95 (*J* 12.5 Hz). Attempted isolation of pure *cis*-isomers has not so far been successful, using preparative TLC or medium-pressure column chromatography on silica gel. Rapid *cis*-to-*trans*-isomerisation takes place on the columns or plates. Each of the compounds 5–11 is, however, reasonably thermally stable in the *cis*-form; solid samples of mixtures of *cis*- and *trans*-isomers could be stored at room temperature without change for several weeks when kept in the dark.

Reduction potentials were determined by cyclic voltammetry and are given in Table 1. Both first and second

1; R = Et
2; R = [CH$_2$]$_5$CO$_2$H

3

4

5, X = H   9, X = Br
6, X = Me   10, X = F
7, X = MeO   11, X = CN
8, X = Cl

Scheme 1 *Reagents and conditions:* i, Ph$_3$PH$^+$Br$^-$, C$_6$H$_6$; ii, aq. NaOH, CH$_2$Cl$_2$; iii, ArCHO, CH$_2$Cl$_2$; iv, I$_2$, toluene, reflux

Table 1 Electrochemical parameters[a] (E in V) and *trans*:*cis* ratios for 2-(2-arylvinyl)-9,10-anthraquinones **5–11**

Compound	*trans*			*trans*–*cis*-Mixtures		
	$-E_{p,c}(1)$	$-E_{p,c}(2)$	n/F mol^{-1}	$-E_{p,c}(1)$	$-E_{p,c}(2)$	*trans*:*cis*[b]
5	0.93	1.48	1.95	0.85	1.45	77:23
6	0.88	1.43	1.91	0.80	1.37	58:42
7	0.84	1.42	1.89	0.75	1.40	36:64
8	0.85	1.40	1.95	0.91	1.42	49:51
9	0.99	1.56	1.85	0.82	1.43	37:63
10	0.90	1.49	1.95	1.04	1.55	58:42
11	(0.58	1.18)[c]	2.2	0.85	1.42	42:58
5	(0.57	1.28)[c]	—	—	—	—

[a] Cyclic voltammetry at a vitreous carbon cathode: MeCN–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}); 0.2 V s^{-1}; substrate 10^{-3}–10^{-4} mol dm^{-3}; reference, Ag/AgI; both waves reversible, oxidation peak potentials not given here. Controlled potential coulometry at $E_{p,c}(1)$; Hg cathode; DMF-Bu$_4$NI (0.1 mol dm^{-3}); Ag/AgI reference; PhCO$_2$H proton donor ($\times$2). [b] Irradiation of the *trans*-isomer in CH$_2$Cl$_2$ solution in a water-jacketed Pyrex cell with an Hg arc UV lamp (Cathodem Ltd., type 7833) for 90 min. Isomer ratios determined by ^{1}H NMR spectroscopy (see text). [c] DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}).
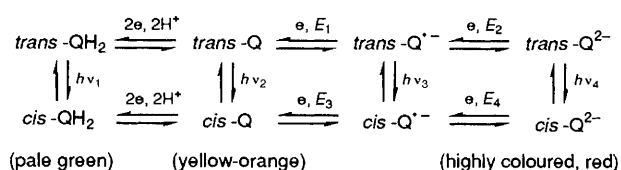
Scheme 2 Q = quinone form of compounds **5–11**

reduction waves are reversible and diffusion-controlled, and are characteristic of the anthraquinone function. Radical-ions are formed at modest potentials and these potentials are little affected by substitution at the 4'-position in the stilbene part of the molecule. In the presence of proton donor (benzoic acid) the first wave becomes irreversible and the peak current is doubled. Controlled potential coulometry experiments under these conditions (Table 1) indicate that each of the compounds **5–11** undergoes smooth 2 F mol^{-1} reduction. The cyclic voltammetry of solutions of mixtures of the *cis*- and *trans*-isomers is closely similar to that of the corresponding *trans*-isomers. The reduction peaks are generally broader but there is no resolution indicating significantly different potentials for the two series of isomers.

Conversion of the *trans*-series of compounds into the corresponding quinols (*trans*-QH$_2$ in Scheme 2) was achieved both chemically (sodium hydrogensulfite–ethanol) and by controlled potential electrolysis at $E_{p,c}(1)$ in DMF-Bu$_4$NBF$_4$ (0.1 mol dm^{-3})–PhCO$_2$H (2 equiv.) and at a mercury pool cathode. In each method it was necessary to keep the reaction solutions under nitrogen. The pale green hydroquinones could be isolated as crystals from the chemical reductions and although they rapidly oxidised in air they could be kept as solids under nitrogen. In the electrolyses the current fell to the background value typically at *ca.* 1.9 F mol^{-1} and pale-green, fluorescent solutions were obtained. With normal aqueous work-up the starting quinones were isolated, an indication of the ease of re-oxidation.

It was important to establish whether or not *cis*-to-*trans*-isomerisation took place during electrolysis. Consequently a mixture (*ca.* 1:1) of the *cis*- and *trans*-isomers of **10** (X = F) was cathodically reduced, as above, to give a pale-green solution which was diluted with water and the product extracted into chloroform. The starting compound was recovered quantitatively and most significantly with no detectable change in the *trans*:*cis* ratio. The radical-anions at least are configurationally stable under the conditions of electrolysis.

UV spectra were measured for the *trans*-series for solutions in acetonitrile. Four bands were observed in the region 245–412 nm, depending on substitution. The lower wavelength bands [*ca.* 245 (λ_1) and 275 nm (λ_2)] varied little

with substitution but the higher wavelength bands (λ_3 and λ_4) were more sensitive to the nature of X. For instance, for **5** (X = H) λ_3 = 306 nm and λ_4 = 389 nm with ϵ = 20 181 and 5 890 dm^3 mol^{-1} cm^{-1} respectively; values for **7** (X = MeO) λ_3 = 320 nm (ϵ 26 554), λ_4 = 412 nm (ϵ 10 846 dm^3 mol^{-1} cm^{-1}). This illustrates the range of values found for compounds **5–11**. Because pure samples of the *cis*-isomers were not obtained their UV spectroscopic parameters were determined by measurement on a mixture of isomers of known composition with instrumental subtraction of the spectrum of the pure *trans*-sample. For instance, for *cis*- **5** λ_3 = 336 nm and λ_4 = 450 nm and absorbance values are reduced about fifteenfold; there are significant bathochromic shifts for *cis* vs. *trans* of $\Delta\lambda_3$ = 30 and $\Delta\lambda_4$ = 61 nm. It is intended to determine the corresponding parameters for the radical-anions and dianions and also to pursue the isolation of samples of pure *cis*-isomers.

It is clear from this work that compounds of the type **5–7** are: (*i*) easily prepared; (*ii*) convertible electrochemically into 1e and 2e reduction states; and (*iii*) further converted photochemically into thermally and electrochemically stable and distinguishable *cis*- and *trans*-states. In addition a variety of substitution greater than that so far explored is accessible and should allow relatively easy attachment to other materials, *e.g.* polymer films, as a prelude to their use in displays or information storage.

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