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Relationships between Spectroscopic and Voltammetric Parameters of Azobenzene Dyes

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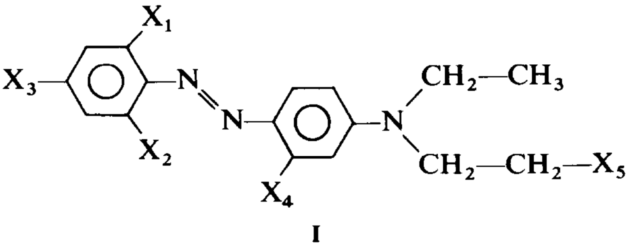
ABSTRACT

Voltammetric reduction on a hanging mercury electrode in aprotic and anhydrous medium was performed for a series of azobenzene dyes. The effects of substituents on both the aromatic rings and the N,N-*diethylamino chain have been investigated, thus yielding correlations of reduction potentials with absorption maxima of dyes and their* ^{13}C *nuclear magnetic resonance (NMR) chemical shifts.*

INTRODUCTION

In previous papers, the structure–activity relationships of a series of substituted dialkylamino-azobenzenes have been studied using statistical methods.[1–4] In this study, the voltammetric reduction in aprotic and anhydrous medium of a series of compounds of general formula **I**, whose structures are detailed in Table 1, has been investigated. The voltammetric



I

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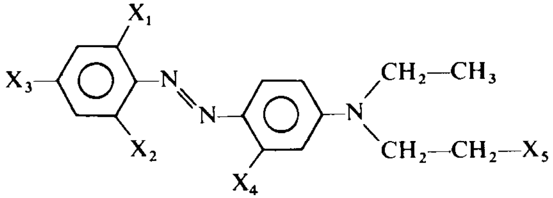
TABLE 1
Electrochemical and Spectral Data of Dyes **1**–**16**



Compound number	*Structure*					$E^1_{1/2}$ $(V)^a$	ΔE $(mV)^b$	$\frac{I_a}{I_c}$	E^2_p $(V)^c$	λ_{max} *(nm)*
	X_1	X_2	X_3	X_4	X_5					
1	H	H	H	H	H	−1·528	65	0·9	−2·150	416
2	H	H	H	H	CN	−1·488	76	1·0	−2·108	402
3	H	H	H	H	OH	−1·542	72	0·7	−2·164	418
4	H	H	CN	H	H	−1·207	73	1·0	−1·671	462
5	H	H	OCH_3	H	H	−1·635	90	0·9	−2·235	412
6	H	H	CN	H	CN	−1·175	68	1·0	−1·679	435
7	H	H	OCH_3	H	CN	−1·550	80	1·0	−2·217	405
8	H	H	CN	$NHCOCH_3$	H	−1·122	74	1·0	−1·476	487
9	Cl	H	H	H	CN	−1·337	70	1·0	−1·944	414
10	OCH_3	H	NO_2	$NHCOCH_2CN$	H	−0·920	95	0·8	−1·355	518
11	CN	H	H	$NHCOCH_3$	H	−1·111	66	0·8	−1·409	484
12	Br	Cl	NO_2	H	H	−1·101	92	1·0	−1·470	446
13	CN	H	H	CH_3	H	−1·252	73	1·0	−1·819	467
14	H	H	CN	CH_3	H	−1·224	70	1·0	−1·694	470
15	Br	Cl	NO_2	CH_3	CN	−1·140	90	1·0	—	434
16	H	H	NO_2	H	H	−1·291	78	1·0	—	485

[a] First wave
[b] $\Delta E = E^1_{pa} - E^1_{pc}$.
[c] Second wave.

parameters were found to be related to some spectroscopic properties of the dyes.

The mechanism of the reduction of azobenzenes has been shown to depend on the solvent and on dye structure.[5–11] In aprotic and anhydrous solvents the voltammetric curves show a first reversible wave, in agreement with the mechanism represented by eqns (1)–(3):[12]

$$\mathrm{Ar{-}N{=}N{-}Ar} + e^- \rightleftharpoons [\mathrm{Ar{-}N{=}N{-}Ar}]^{\cdot -} \qquad (1)$$

$$[\mathrm{Ar{-}N{=}N{-}Ar}]^{\cdot -} + e^- \rightleftharpoons [\mathrm{Ar{-}N{=}N{-}Ar}]^{2-} \qquad (2)$$

$$[\mathrm{Ar{-}N{=}N{-}Ar}]^{2-} + \mathrm{HS} \longrightarrow [\mathrm{HAr{-}N{=}N{-}Ar}]^- + \mathrm{S}^- \qquad (3)$$

where HS represents any source of proton donors.

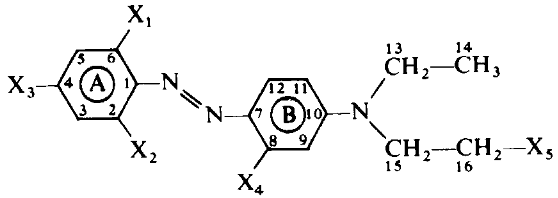
The second wave is usually irreversible, as a consequence of the protonation of the dianion. If electron-withdrawing substituents are present, the dianion is more stable and the wave is reversible. The process is considerably altered by the presence of proton donors at high concentrations, viz. water. In these conditions, the radical-anion is protonated and can consequently be reduced at more anodic potentials than the starting azo dye. When the concentration of the proton donors is sufficiently high, the first wave corresponds to a two-electron reduction and the second disappears. For a given concentration of the dye, the proton donor concentration at which the above effects are observed depends on the acidity of the donor and on the structural stabilization of the radical-anion.

EXPERIMENTAL

The voltammetric measurements were performed with an Amel 433 polarograph connected to an IBM/AT computer. All the potentials are quoted with respect to the Ag/AgCl reference electrode, using a platinum wire auxiliary electrode and a static mercury drop working electrode. The acetonitrile solutions (0·1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte) were dried on an activated neutral alumina column. The alumina (Merck activity grade 1) was activated by heating for 12 h at 350°C in vacuum, cooled and stored in a desiccator over phosphorus pentoxide. The dye concentration was 1×10^{-3} M. The temperature was 25 ± 0·5°C. The scan rate was varied in the range 0·1–2·0 V/s. The dyes have been previously described.[1] ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 solution (dye concentration 0·2 M) on a Jeol GX-270 spectrometer, using the solvent signal (39·60 ppm) as internal standard. The conditions of measurement were as follows: number of data points, 32 K; spectral width, 18 kHz; cycle times, 2–3 s; number of transients, 1000–5000;

TABLE 2

^{13}C Chemical Shifts (ppm)



Compound number	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*	*C-12*	*C-13*	*C-14*	*C-15*	*C-16*
1	152·58	121·77	129·20	129·39	129·20	121·77	142·15	125·16	111·00	150·15	111·00	125·16	44·09	12·54	44·09	12·54
2[a]	152·48	121·96	129·33	129·81	129·33	121·96	142·91	125·04	111·73	149·73	111·73	125·04	44·58	12·18	45·52	15·86
3[a]	152·56	121·82	129·24	129·47	129·24	121·82	142·23	125·08	111·16	150·65	111·16	125·08	45·15	12·08	52·20	58·41
4[a]	154·70	122·40	133·57	110·81	133·57	122·40	142·30	126·13	111·21	151·12	111·21	126·13	44·27	12·57	44·27	12·57
5	146·73	123·49	114·44	160·49	114·44	123·49	142·12	124·74	111·02	149·64	111·02	124·74	44·08	12·80	44·08	12·80
6[a]	154·82	122·51	133·61	111·24	133·61	122·51	143·01	125·84	111·86	150·71	111·86	125·84	44·64	12·15	45·49	15·83
7[a]	146·61	123·62	114·44	160·72	114·44	123·62	142·91	124·51	111·70	149·11	111·70	124·51	44·51	12·15	45·52	15·83
8[a]	154·96	122·53	133·40	110·29	133·40	122·53	131·13	139·48	101·04	151·06	107·60	122·53	44·56	12·60	44·56	12·60
9[a]	148·41	117·47	127·95	130·78	130·54	132·76	143·32	125·60	111·81	150·26	111·81	125·60	44·64	12·16	45·50	15·83
10	145·21	115·98	115·98	147·28	107·95	154·72	131·74	136·61	100·89	151·77	107·78	128·13	44·40	12·25	44·40	12·25
11[a]	153·96	119·60	134·21	128·87	134·09	107·19	130·72	139·28	100·67	152·55	107·94	124·61	44·79	12·71	44·79	12·71
12	154·31	126·15	127·33	145·57	125·17	116·11	141·97	126·41	111·31	152·00	111·31	125·17	44·47	12·57	44·47	12·57
13[a]	154·28	117·96	133·95	128·94	133·82	109·30	142·90	140·66	111·78	151·36	110·14	117·60	44·17	12·65	44·17	12·65
14[a]	155·43	122·35	133·48	110·37	133·48	122·35	142·67	140·68	111·76	151·15	109·90	117·41	44·11	12·63	44·11	12·63
15[a]	154·31	126·57	127·70	145·75	125·53	116·53	143·66	141·63	112·75	152·00	110·85	117·86	44·97	12·57	45·67	16·17
16[a]	156·33	122·27	124·78	146·71	124·78	122·27	142·50	126·15	111·26	151·31	111·26	126·15	44·17	12·41	44·17	12·41

[a] Ref. 13.

flip angles, 45°; line broadening factor, 0·8; sample speed rotation, 15 Hz. The NMR data are reported in Table 2. Electronic absorption spectra in methanol were recorded on a Pye–Unicam SP 8-100 spectrophotometer.

RESULTS AND DISCUSSION

The general shape of the voltammetric reduction curves is shown in Fig. 1(a) for dye **1** (diethylamino-azobenzene). The reduction peaks of the first and the second wave are present at −1·561 and −2·150 V, respectively. The first wave is accompanied by the corresponding oxidation wave at −1·496 V. In the second wave, during the scan towards anodic potentials, no oxidation signals are detected. An oxidation wave is, however, present at about −1·20 V, and absent if the inversion potential is less cathodic than the second wave (Fig. 1(b)). It follows that the peak is due to the oxidation of the product formed by the irreversible reduction process of the second wave. In agreement with a reversible reduction mechanism ruled by diffusive processes, the peak potential of the first wave does not change as the scan rate changes (0·1–2·0 V/s), and the I_p vs $\sqrt{v}$ plot is linear (Fig. 2).

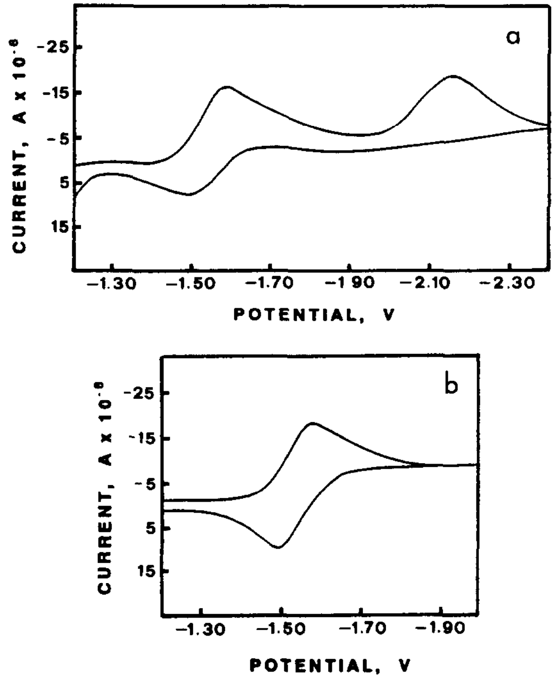


Fig. 1. Voltammogram of dye 1. (a) Scan range −1·20 to −2·40 V; (b) scan range −1·20 to −1·90 V.

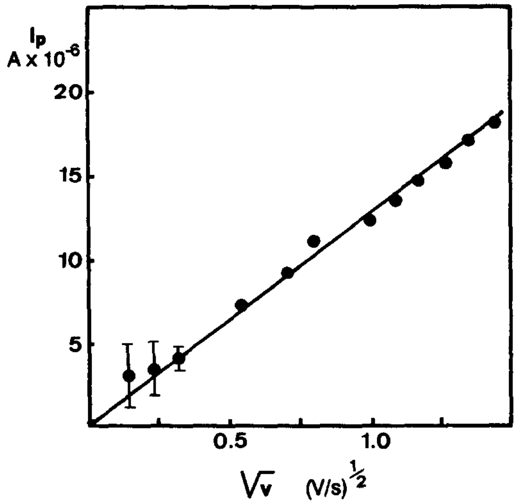


Fig. 2. Plot of peak current (I_p) vs scan rate ($\sqrt{v}$) for dye 1.

The presence of water alters the voltammetric behaviour, as shown in Fig. 3. The position of the first wave is substantially unchanged, as the second wave is anodically shifted by increasing water concentration. At the same time, during the cathodic scan, the intensity of the first wave increases to the detriment of the second. During the anodic scan the intensity of the first anodic wave is lowered. The above general trend is a peculiarity of the whole series of dyes. Each of the dyes has a different susceptibility to water. For monosubstituted dyes (X_3 = CN, H, OCH_3) water/dye molar ratios of 700, 170 and 110, respectively, are required, to give a mono-wave irreversible voltammetric curve. In the presence of water, the peak potentials do not

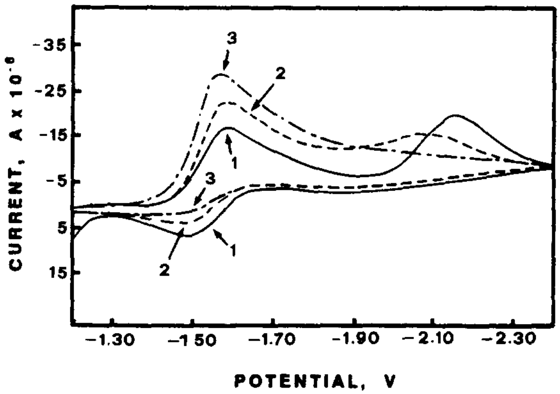


Fig. 3. Voltammogram of dye I at various water/dye ratios: 1 (——), 0; 2 (– – –), 100; 3 (—·—), 150.

remain constant as the scan rate varies, in agreement with irreversible reduction processes following post-electrode reactions.

The presence of substituents on both the aromatic rings and at the X_5 position affects the reduction potentials. Table 1 shows λ_{max} values, together with $E^1_{1/2}$ (mean values of cathodic and anodic peaks of the first wave), I_p anodic/I_p cathodic ratios and $\Delta E(E_c - E_a)$. The I_p ratios are not far from unity. Lower values are shown by compounds with substituents containing active hydrogens (OH and NHCOR). These may partially function as proton donors, thus giving rise to post-electrode reactions on the radical-anion.

ΔE values are in the range 65–95 mV. Dyes containing the methoxy group (**5** and **7**) or polysubstituted in ring A (**10**, **12** and **15**) more markedly differ from the theoretical case of a mono-electron reversible mechanism, viz. $\Delta E = 59$ mV. Probably the electron donor OCH_3 group lowers the stability of the radical-anion, whereas the crowding of substituents near the azo group reduces the electronic delocalization. Furthermore, in compounds **10**, **12** and **15**, the presence of the nitro group gives rise to additional reduction waves at more positive potentials (−0·78, −0·75 and −0·76 V). As a consequence, the waves are not due to radical-anions, but to less stable and more reactive dianions.

The substituents in aromatic rings shift reduction potentials towards less negative values as their electron attracting power (related to Hammett σ_p constants) increases. Figure 4 shows, as examples, values of X_3 substituted dyes ($X_3 = OCH_3$, H, CN). The cyano substituent on the side-chain (X_5) exerts an analogous but less intense effect, as shown by pairs **5**–**7**, **1**–**2** and **4**–**6**.

It is well known that reduction potentials are related to energy levels of the first non-bonding orbital and, consequently, to the position of the

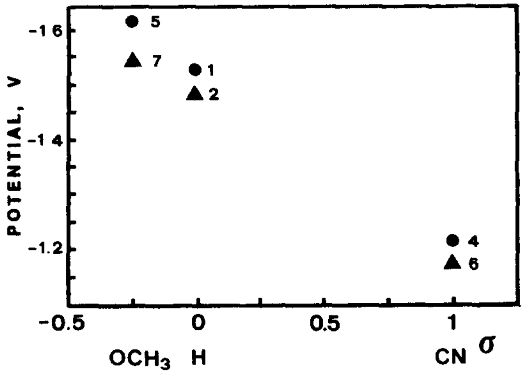


Fig. 4. Plot of $E_{1/2}$ vs Hammett σ constants for X_3 substituted dyes. Compound numbers as in Table 1.

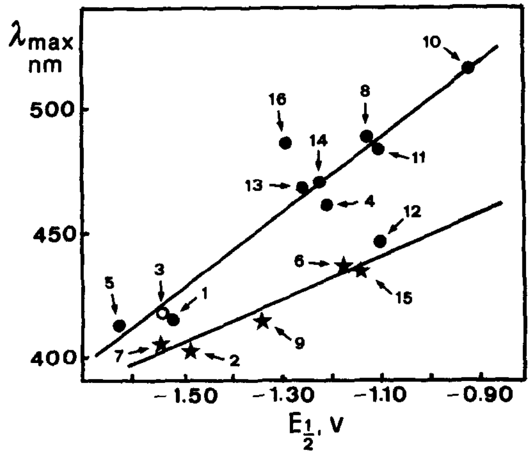


Fig. 5. Plot of absorption maxima of dyes (compound numbers as in Table 1) vs $E_{1/2}$.

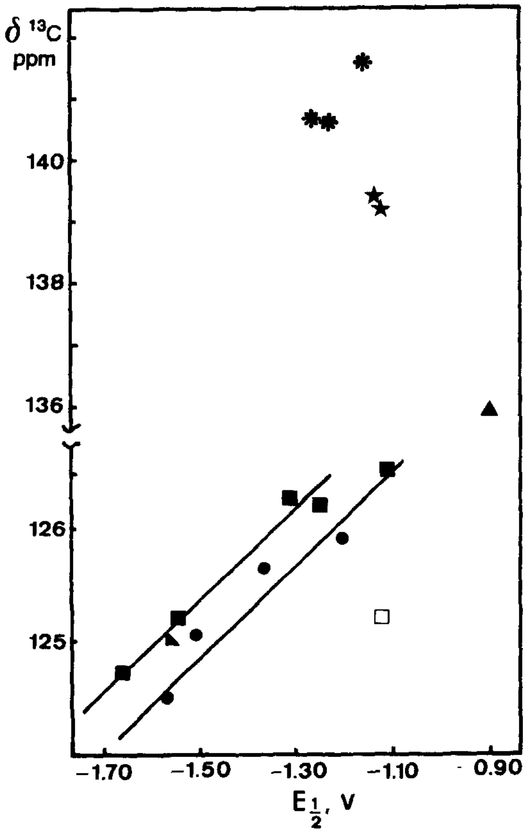


Fig. 6. Plot of ^{13}C NMR chemical shifts of C-8 vs $E_{1/2}$. ■, $X_5 = H$; ●, $X_5 = CN$; ◣, $X_5 = OH$; ∗, $X_4 = CH_3$; ★, $X_4 = NHCOCH_3$; ▲, $X_4 = NHCOCH_2CN$; □, incorrect assignment for dye **12**.

absorption maxima in electronic spectra. An approximately linear correlation between absorption maxima of dyes and first wave potentials has been found ($r = 0{\cdot}806$). Considering the far from negligible effect of the CN substituent in X_5, the dyes were grouped into two sub-classes based on the presence or absence of the cyano group, thus giving an improvement in the linear correlations shown in Fig. 5 ($r_{X_5=H} = 0{\cdot}887$; $r_{X_5=CN} = 0{\cdot}968$). The outliers **12** and **16** are still evident and the regression is further improved if these are omitted ($r_{X_5=H} = 0{\cdot}991$). This behaviour may be explained by the interference of more easily reducible nitro groups.

The ^{13}C NMR chemical shifts are also related to $E_{1/2}$ values.[14,15] The chemical shifts of individual carbon atoms are strongly influenced by 'ipso' substituents. Meanwhile, groups in other positions variably affect the chemical shifts. On the other hand, the reduction potential depends on the substituents' effect as a whole. For these reasons, i.e. the high degree of substitution of the A ring, the carbon atoms in the ring are only involved in poor correlations.

More significant relationships are found for the carbon atoms in ring B and in the side-chains. Figure 6 shows the plot of C-8 chemical shift values vs $E_{1/2}$. Two families are evident; the first has substituents (CH_3, NHCOR) in the 8 position ('ipso') and the second is unsubstituted. Furthermore, the points of the second family may be grouped into two sub-classes, based on the presence or absence of the cyano group in X_5 (the dye with $X_5 = OH$ seems to belong to the $X_5 = H$ sub-class). This correlation proved to be a good tool for solving an assignment problem. In fact, for dye **12**, inspection

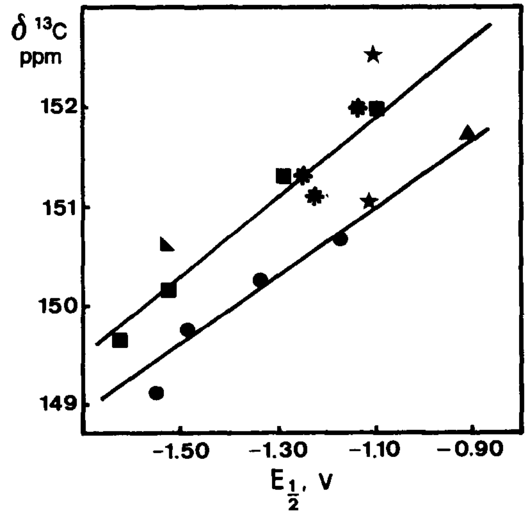


Fig. 7. Plot of ^{13}C NMR chemical shifts of C-10 vs $E_{1/2}$. ■, $X_5 = H$; ●, $X_5 = CN$; ◣, $X_5 = OH$; ∗, $X_4 = CH_3$; ★, $X_4 = NHCOCH_3$; ▲, $X_4 = NHCOCH_2CN$.

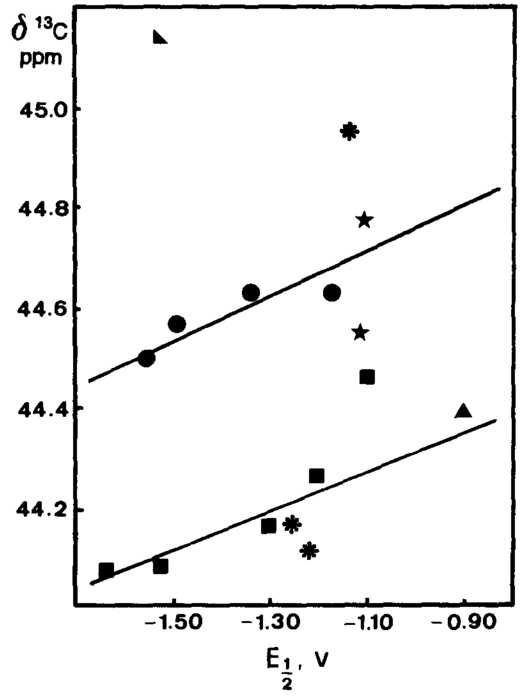


Fig. 8. Plot of ^{13}C NMR chemical shifts of C-13 vs $E_{1/2}$. ■, $X_5 = H$; ●, $X_5 = CN$; ◣, $X_5 = OH$; *, $X_4 = CH_3$; ★, $X_4 = NHCOCH_3$; ▲, $X_4 = NHCOCH_2CN$.

of the spectra would firmly indicate C-5 at 126·41 and C-8 at 125·17 ppm. From Fig. 6 the correct assignment of C-8 at 126·41 ppm (and not at 125·17 ppm) is unambiguous.

Figure 7 (C-10) shows the presence or the absence of CN in X_5, whereas substituents in X_4 give rise to a spread of points through the two sub-classes. Finally, the carbon atoms of the alkyl chains (Fig. 8, C-13), even if less susceptible to substituent effects, again indicate two sub-classes governed by X_5 substitution, and a spread of points if X_4 substituents are considered.

CONCLUSIONS

The structure of diethylamino-azobenzene dyes and the type of reaction medium are important factors in determining the electrochemical reduction processes and the shapes of the related curves. The peak potentials of the first cathodic wave are linearly correlated with spectroscopic parameters such as the absorption maxima of dyes in solution and the ^{13}C NMR chemical shifts of selected dyes and carbon atoms. The correlations, in turn, may be used as a tool for unambiguous assignments of spectroscopic parameters.

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