POLAROGRAPHIC BEHAVIOUR AND PHYSICO-CHEMICAL CHARACTERISTICS OF SOME 5-ARYLAZOPYRIMIDINES OF BIOLOGICAL SIGNIFICANCE

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The polarographic behaviour of a series of the title compounds has been investigated in aqueous alcoholic buffered media and in DMF–0.1M-$LiClO_4$. A mechanism interpreting the electrode process was suggested and confirmed via the identification of CPE products, the use of models and the Hammett's σ–$E_{1/2}$ relationship. The different physico-chemical characteristics of these compounds were also determined. A linear correlation was shown to exist between their redox potentials and spectroscopic data.

The synthesis of arylazopyrimidines has been the subject of recent interest in pharmacological activities[1-3]. Central nervous system depressor, tranquilizer, anticoagulant, antitumour, antineoplastic and antiinflammatory properties have been found for some members of these compounds. Whereas much research has been directed to the study of the electrochemistry and spectroscopy of pyrimidines[4-8], only very little attention was paid to the polarography of 2-amino-5-arylazopyrimidines. Goyal et al.[9] reported preliminary polarographic results of some 5-arylazopyrimidines observing one wave which represents 2-electron step. In the present investigation the polarographic behaviour of 2-amino-4,6-dialkyl-5-arylazopyrimidines (*Ia – Il*) in ethanolic–buffer solutions as well as in DMF–0.1M-$LiClO_4$ solution has been studied. The results of the present study were focussed on the following objectives:

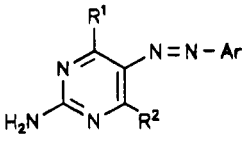
1. To elucidate the mechanism of electroreduction and oxidation of the compounds *Ia – Il* at the dropping mercury electrode (DME).

2. To estimate their different physico-chemical characteristics viz., diffusion coefficient (D), dissociation constant (pK_a), redox potential ($\Delta E_{1/2}$), electron affinity (EA), ionization potential (IP), electronic transition energy (E_{CT}) and coulomb repulsion integral (J_{12}).

3. To find out a simple electrochemical route for the synthesis of related compounds through a study of their controlled potential electrolysis (CPE).

4. To investigate the effect of substituents (in the heterocyclic ring or phenyl group) on the actual electrochemical reduction mechanism through the application of Hammett's linear free energy relationships.

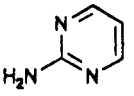
For comparison, the polarographic behaviour of pyrimidine (*II*), 2-aminopyrimidine (*III*) and 2-amino-4,6-dimethylpyrimidine (*IV*) were studied as well under the same conditions, as simple model compounds.



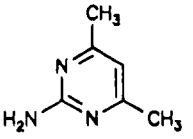
I

	R^1	R^2	Ar
a	Me	Me	C_6H_5
b	Me	Me	*m*-C_6H_4Cl
c	Me	Me	*p*-C_6H_4Cl
d	Me	Me	*m*-C_6H_4Br
e	Me	Me	*p*-C_6H_4Br
f	Me	Me	*m*-$C_6H_4CH_3$
g	Me	Me	*p*-$C_6H_4CH_3$
h	Me	Me	*m*-$C_6H_4OCH_3$
i	Me	Me	*p*-$C_6H_4OCH_3$
j	Me	Ph	C_6H_5
k	Ph	Ph	C_6H_5
l	Me	Me	*p*-$C_6H_4NO_2$

II



III



IV

EXPERIMENTAL

Organic Synthesis

5-Arylazopyrimidines (*Ia* – *Il*) were prepared according to literature[10] by the condensation of guanidine nitrate with appropriately substituted 2,3,4-pentanetrione-3-arylhydrazones. The solids were purified by recrystallization from ethanol and their purity and structure were checked by measurements of m.p., IR, mass spectra and elemental analysis.

Polarographic Investigation

Apparatus. Polarographic curves were recorded with a Sargent polarograph Model XVI. A cell of our own design with a separated saturated calomel electrode (SCE) was used[11]. The capillary had the following characteristics in open circuit: t = 4.35 s, m = 1.98 mg s^{-1} for h = 51 cm. For controlled potential electrolysis (CPE), an ASA 100 Tacussel potentiostat was used. The amount of electricity consumed during electrolysis was measured with an electronic Tacussel integrator type 1G3A.

Measurements. All experiments were carried out at 25 ± 0.1 °C. The half-wave potentials ($E_{1/2}$) were measured graphically and expressed versus SCE with an accuracy of ±0.005 V.

Procedure. Depolarizer concentrations were 5 . 10^{-4} mol l^{-1} in 50% (v/v) ethanolic–Thiel buffer mixtures and in DMF–0.1M-$LiClO_4$ solution. Prior to each run, pure nitrogen gas was bubbled through the polarographic cell. At pH < 7, the polarogram is distorted by a maximum which can be eliminated by the addition of 0.01% gelatine.

Controlled Potential Electrolysis and the Identification of the Resulting Products

An amount of 40 ml of 50% ethanolic–buffer solution were introduced into the cell. After dearation of the solution with a stream of pure N_2, the compound *Ia* (8.52 mg) was then introduced. The electrolysis starts at a potential corresponding to the limiting current plateau (–0.6 V). The progress of electrolysis was followed by recording polarograms at 3.6 coulombs intervals (theoretical value for one electron process). The electrolysis was completed after the passage of 14.4 coulombs equivalent to 4 F per mol, and the resulting solution was evaporated to 1/3 of its original volume. The organic substances were then extracted with dry ether and the solvent removed in vacuo. The obtained mixture was treated with water. The insoluble part was isolated by filtration and identified as 2,5-diamino-4,6-dimethylpyrimidine (iv) by m.p., elemental analysis, NMR and IR spectra. The soluble part was concentrated by evaporation and the presence of aniline in the solution was revealed by standard spot test[12].

Determination of the Acid Dissociation Constants

The pK_a values of the studied compounds were evaluated spectrophotometrically[13] in 50% ethanolic–buffer solutions at ionic strength of 0.1 mol l^{-1} and 25 ± 0.1 °C. The electronic absorption spectra were measured on a Pye–Unicam SP 8000 instrument.

RESULTS AND DISCUSSION

Polarographic Behaviour of Ia – Il

With the exception of compound *Il*, all the polarograms of the other members of the series studied showed one well-defined polarographic wave A which was predominant throughout the whole pH range (Fig. 1). In addition to wave A compound *Il* displayed another wave B at a more negative potential. Comparison of the polarograms of *Il* with those of *Ia – Ik* indicates that this wave is most probably due to the nitro group occupying the para position. Also, a wave-height ratio comparison with wave A indicates that wave B is a 4-electron step and the $E_{1/2}$–pH plot of B seems to be compatible with those reported for the reduction of aromatic nitro compounds to the hydroxylamine derivatives[14], following the equation $E^{b}_{1/2}$ = –0.187 – 0.084 pH. In the pH range 4.3 – 6.4

and above 10, compound *II* exhibited another wave C with a limiting current equal to 2e where its $E_{1/2}$ is pH-independent. This wave can be considered as representing further reduction of the –NHOH group into the amino group[11,14].

Nature of Wave A

Routine analysis of wave A through the effect of concentration and height of mercury column showed that this wave is diffusion-controlled. Cyclic voltammetry using a hanging mercury drop at different sweep rates (Fig. 2) together with logarithmic analysis indicated that the process is irreversible in nature. This was also substantiated by the shift of $E_{1/2}$ towards negative values as the concentration of the depolarizer increased[15]. The irreversibility of the process was further checked by determining the heterogeneous rate constant of the forward reaction ($k^0_{f,h}$) using the relations reported by Meites and Israel[16]. The variation of the value of $k^0_{f,h}$ in the range 10^{-4} – 10^{-12} in the pH limits 2 – 11 indicates that the irreversibility of the electrode process increases with increasing pH. The higher values of the activation free energy (ΔG^*), being calculated by applying the different approaches proposed for the analysis of irreversible waves[17 - 19] confirm such irreversibility. The diffusion coefficient D of the depolarizer was determined experimentally by applying the Stokes–Einstein equation[20], $D = 3.32 \cdot 10^{-5} (d/M)^{1/3} / \eta$, $cm^2 s^{-1}$.

It is evident from Fig. 3 that the shift of $E_{1/2}$ with the increase in pH can be described by a straight line up to pH ≈ 10 above which the $E_{1/2}$–pH dependence becomes much less. However, the limiting current seems practically to be pH-independent. Both the

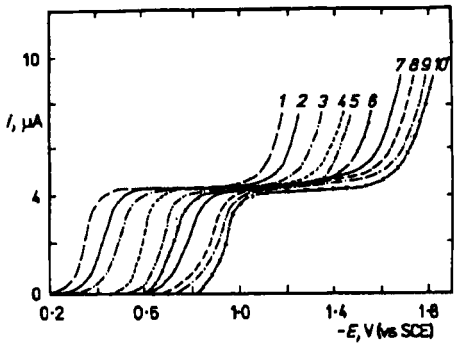


FIG. 1
Polarograms of 5 . 10^{-4}M 2-amino-4,6-dimethyl-5-phenyl-azopyrimidine (*Ia*) in 50% ethanol–Thiel buffer solutions of different values of pH: *1* 2.1, *2* 3.1, *3* 4.3, *4* 5.5, *5* 6.4, *6* 7.3, *7* 8.4, *8* 10.1, *9* 11.5, *10* 12.1

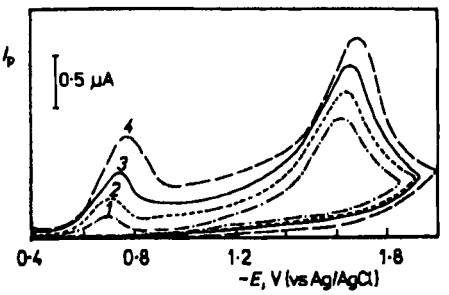
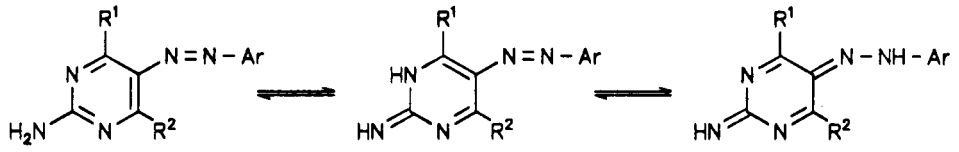


FIG. 2
Cyclic voltammograms of *Ia* at different sweep rates, arylazopyrimidine concentration 1 . 10^{-4}M, pH 6.4; *1* 20, *2* 50, *3* 100, *4* 200 mV s^{-1}

shift of $E_{1/2}$ by an average of 0.068 / pH in the pH range 2 – 10 and the independence of wave height on pH are indications that the molecule is protonated prior to its electrochemical reduction[21]. This finding is also confirmed by applying the equation $dE_{1/2}/dpH = (-2.3\ RT/\alpha nF)\ Z_{H^+}$ which gives the value of hydrogen ions (Z_{H^+}) per molecule[22]. At pH > 10, the shift of $E_{1/2}$ is ≈ 0.035 / pH, which indicate that at such higher pH values, both protonated and unprotonated species are reduced at compatible potentials and moreover the unprotonated form is the predominant one. Table I summarizes the different kinetic parameters calculated from polarographic measurements.

Reduction Mechanism

The possible reduction sites in arylazopyrimidines *Ia – Il* are the cyclic C=N, C=C as well as the exocyclic N=N groups. The proper study of their electrode mechanism necessitates a parallel study of the electroreduction profile of the model compounds namely; pyrimidine (*II*), 2-aminopyrimidine (*III*) and 2-amino-4,6-dimethylpyrimidine (*IV*). The aim is to indicate whether the heterocyclic portion of the molecule is an electroactive site or not. The polarograms of model compounds were measured under exactly the same experimental conditions as for compound *Ia*. Compounds *II* and *III* were proved to be electroactive where their electrode reduction could take place at the 3,4-position to form 3,4-dihydro derivatives which can undergo further reduction to the corresponding tetrahydro derivative in case of pyrimidine (*II*) only; the finding being similar to that of Smith et al.[5]. On the other hand, the compound *IV* shows no reduction waves along the whole studied pH range. It is evident, therefore, that in the compounds *Ia – Il* while the pyrimidine ring is electroinactive, the center N=N is expected to be the active one. Moreover, these compounds may have one of the following potentially tautomeric structures $I_\alpha - I_\gamma$ i.e., the active center may exist in the azo or in the hydrazono form;



Iα *Iβ* *Iγ*

The protonation of pyrimidine *II* and 2-aminopyrimidine *III* increases, most probably, their electron deficiency character enhancing thereby their ability towards the electroreduction. The ease of reduction of the pyrimidine ring decreases with the increase in the number of added electron donating substituents. The effect of these substituents seems to involve saturation of the ring by means of tautomeric shifts

TABLE I
Polarographic results obtained for some 2-amino-5-arylazopyrimidines

Compound	pH	$-E^{s}_{1/2}$	$10^6 D$ $cm^2 s^{-1}$	S^s	αn	$\Delta E_{1/2}/\Delta pH$	Z_{H^+}	$k^0_{f,h}$ $cm\ s^{-1}$	ΔG^* $kJ\ mol^{-1}$
Ia	2.1	0.34	2.427	15.97	0.94	0.067	1.07	$2.4 . 10^{-4}$	304.51
	5.3	0.56		15.67	0.92		1.07	$4.3 . 10^{-9}$	411.27
	11.5	0.93		12.29	0.72	0.035	0.43	$5.1 . 10^{-11}$	438.92
Ib	2.1	0.35	2.621	14.41	0.85	0.068	0.98	$3.6 . 10^{-4}$	315.22
	5.3	0.58		14.26	0.84		0.97	$5.5 . 10^{-10}$	432.17
	11.5	0.96		12.35	0.73	0.034	0.42	$2.8 . 10^{-12}$	477.05
Ic	2.1	0.29	2.714	14.11	0.82	0.068	0.96	$1.4 . 10^{-4}$	300.54
	5.3	0.50		13.53	0.80		0.92	$3.9 . 10^{-9}$	403.29
	11.5	0.89		11.14	0.66	0.035	0.39	$6.8 . 10^{-11}$	422.16
Id	2.1	0.31	3.052	14.01	0.83	0.066	0.93	$4.1 . 10^{-4}$	309.13
	5.3	0.54		13.33	0.79		0.88	$1.1 . 10^{-9}$	410.19
	11.5	0.91		11.21	0.66	0.033	0.37	$2.7 . 10^{-11}$	422.87
Ie	2.1	0.27	2.897	15.29	0.90	0.068	1.04	$8.3 . 10^{-4}$	289.14
	5.3	0.48		13.53	0.80		0.92	$2.7 . 10^{-8}$	384.51
	11.5	0.84		11.47	0.68	0.034	0.39	$3.3 . 10^{-10}$	409.97
Ig	2.1	0.29	2.312	15.44	0.91	0.068	1.05	$1.9 . 10^{-4}$	300.38
	5.3	0.52		14.56	0.86		0.99	$2.4 . 10^{-9}$	422.15
	11.5	0.90		12.57	0.74	0.035	0.44	$9.1 . 10^{-11}$	481.92
Ii	2.1	0.33	2.947	16.47	0.97	0.068	1.12	$2.1 . 10^{-4}$	301.21
	5.3	0.54		15.15	0.89		1.03	$4.4 . 10^{-9}$	409.94
	11.5	0.91		14.17	0.84	0.036	0.51	$5.8 . 10^{-11}$	439.29
Ij	2.1	0.28	3.043	14.63	0.86	0.067	0.98	$4.7 . 10^{-4}$	265.93
	5.3	0.50		13.58	0.80		0.91	$2.1 . 10^{-8}$	379.77
	11.5	0.90		13.94	0.82	0.033	0.46	$3.9 . 10^{-10}$	410.43
Ik	2.1	0.49	3.029	16.27	0.96	0.067	1.09	$3.3 . 10^{-4}$	329.76
	5.3	0.72		15.37	0.91		1.03	$5.9 . 10^{-10}$	445.22
	11.5	1.05		12.06	0.71	0.034	0.41	$3.8 . 10^{-12}$	489.31
Il	2.1	0.19	2.382	14.26	0.84	0.068	0.97	$2.2 . 10^{-4}$	244.99
	5.3	0.38		13.68	0.81		0.93	$1.7 . 10^{-8}$	303.11
	11.5	0.79		11.43	0.67	0.035	0.40	$6.3 . 10^{-10}$	397.54

through removing possible reduction sites in the ring. The protonation of pyrimidine ring in the compounds *Ia* – *Ik* is expected, therefore, to be difficult taking place most probably at the electroactive azo group. Table II summarizes the pK_a values (10.25 – 11.31) obtained for the compounds *Ia* – *Ik*, which are in a good agreement with the reported data of aromatic azo compounds[23]. However, pK_a values for pyrimidine (1.3), 2-aminopyrimidine (3.54) and 2-amino-4,6-dimethylpyrimidine (4.46) are considerably less than those of the studied series (*Ia* – *Ik*). This may provide an additional evidence for the suggestion that the protonation takes place on the azo moiety. It is, thus, reasonable to conclude that wave A arises from the reduction of an azo (–N=N–) moiety, and not of hydrazono (C=N–NH) form. This conclusion is also supported by the following findings:

TABLE II
Physico-chemical characteristics of some 2-amino-5-arylazopyrimidines (*Ia* – *Ik*)

Compound	pK_a	$-E^{R}_{1/2}$ V	$-E^{OX}_{1/2}$ V	$\Delta E_{1/2}$ V	*EA* eV	*IP* eV	E_{CT} eV	$-J_{12}$ eV
Ia	10.93	0.730	0.208	0.522	1.76	5.51	3.47	2.95
Ib	10.36	0.701	0.177	0.524	1.79	5.56	3.48	2.96
Ic	10.33	0.661	0.130	0.531	1.83	5.63	3.52	2.99
Id	10.25	0.712	0.188	0.524	1.78	5.54	3.48	2.96
Ie	10.30	0.651	0.118	0.533	1.84	5.65	3.53	3.00
If	11.08	0.782	0.272	0.510	1.71	5.42	3.41	2.90
Ig	11.11	0.750	0.234	0.516	1.74	5.48	3.44	2.92
Ih	11.27	0.743	0.223	0.520	1.75	5.49	3.46	2.94
Ii	11.31	0.755	0.237	0.518	1.74	5.47	3.45	2.93
Ij	10.81	0.674	0.143	0.531	1.82	5.61	3.52	2.99
Ik	10.79	0.873	0.367	0.506	1.62	5.28	3.39	2.88

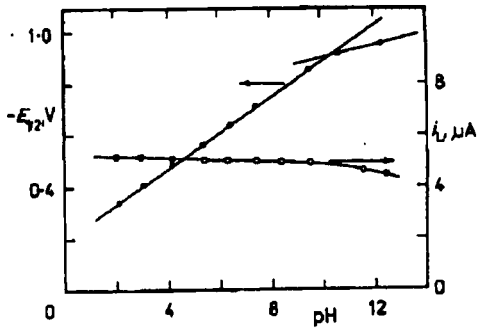


FIG. 3
The correlation of $E_{1/2}$ and i_L of *Ia* with pH

a) The $E_{1/2}$ position and shift in the compounds investigated are very close to those of similar heterocyclic azo and not hydrazono compounds[24,25].

b) The appearance of the reduction wave of the nitro group of compound *II* after the wave A is a direct indication that the reduced species is the azo and not hydrazono form[26].

c) The decrease in height of wave A and its distortion depending upon the changes in methanol concentration, being similar to other azo compounds[27].

From the isolated products and with the help of the obtained polarographic data the following scheme is suggested for the interpretation of the electrochemical reduction of these compounds at the DME,

$$\underset{\text{(i)}}{\text{Y-N=N-Ar}} + \text{H}^+ \rightleftharpoons \underset{\text{(ii)}}{\text{(Y-N=N-Ar) H}^+}$$

$$\text{(ii)} + 2\text{e} + \text{H}^+ \xrightarrow{E_1^a} \underset{\text{(iii)}}{\text{Y-NH-NH-Ar}}$$

$$\text{(iii)} + 2\text{e} + 2\,\text{H}^+ \xrightarrow{E_2^a} \underset{\text{(iv)}}{\text{Y-NH}_2^* + \text{Ar-NH}_2^*}$$

where $E_1^a = E_2^a = E_{1/2}^a =$, Y = 2-amino-4,6-dialkylpyrimidine moiety and * isolated products.

In order to obtain further insight into the proposed mechanism, the most reliable $E_{1/2}$ values at selected pH have been correlated with different Hammett's (σ) constants[28]. Statistical treatment of the data was carried out using Jaffe's calculation[29]. Representative $E_{1/2}$–σ plots (Fig. 4) have reasonable linearity with specific reaction constant (+ρ) values varying between 0.184 – 0.278. These values are in good agreement with those reported previously[30] for arylazo derivatives (0.2 – 0.4) and not for hydrazones (0.05 – 0.2). The positive value of ρ indicates a nucleophilic mechanism (i.e. an electron uptake as potential determining step) and the substituents can affect the reaction center by their inductive effect but not through mesomeric effect. The

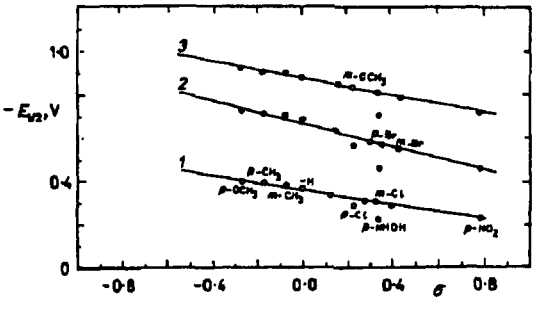


FIG. 4
$E_{1/2}$ –σ relation for compounds (*Ia* – *II*). pH (+ρ) values: *1* 2.1 (0.184); *2* 7.3 (0.278); *3* 11.5 (0.201)

excellent fit using σ for p-NO_2 for the $E_{1/2}$–σ plot and the failure using σ values corresponding to the NO_2 reduction products, NHOH and NH_2, confirms that the azo form is present and reduced prior to the NO_2 group.

Molecular Structure–Reactivity Relationships

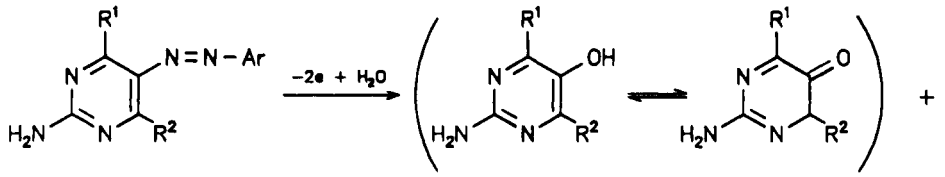
The electronic transition energy (E_{CT}), the half-wave reduction ($E^R_{1/2}$) and oxidation ($E^{OX}_{1/2}$) potentials for compounds *Ia – Ik* have been measured in DMF. The $E^R_{1/2}$ and $E^{OX}_{1/2}$ are used to calculate the electron affinity *EA* and ionization potential *IP*, of these compounds according to the following equations[31 – 33]:

$EA = -E^R_{1/2} + 2.49 \pm 0.26$

$IP = (1.478 \pm 0.027)\, E^{OX}_{1/2} + (5.821 \pm 0.009)$.

Inspecting the values of $E^R_{1/2}$ and E_{CT} for the studied series (Table II), one can conclude that the electron donating substituents render the reduction process more difficult, as indicated from the shift of $E^R_{1/2}$ to more negative values and from the decrease in E_{CT}. On the other hand, the electron attracting groups facilitate the reduction process leading to decrease the delocalization within the whole molecule. An interesting behaviour could be observed on replacing the methyl groups of pyrimidine ring by phenyl groups. For the compound *Ij* where one methyl is replaced by phenyl group, a shift of 0.06 V towards more positive potential was observed as compared with the corresponding compound *Ia*. This can be explained on the basis of electron withdrawing nature of phenyl group, which increases the electron density at the nitrogen atom of the azo group. In compound *Ik*, where two methyl were replaced by phenyl groups, an opposite behaviour was observed. This can be accounted for on the basis of steric hindrance of molecules which varies according to the shape and size of the group[9,34]. Thus, the $E^R_{1/2}$ of *Ik* shifts towards more negative potential and possess lower E_{CT}.

The anodic oxidation of compounds *Ia – Ik* at DME, on the other hand, shows one irreversible diffusion-controlled wave with a height corresponding to 2-electron transfer. From the obtained data one can assume the following oxidation mechanism:



2–amino–4,6–dialkyl–5,6–dihydropyrimidine–5–one

$+ \quad {}^{(+)}N{=}N-Ar \quad + \quad H^{(+)}$

In spite of cathodic behaviour of these compounds, the electron withdrawing substituents shift $E_{1/2}^{OX}$ to more positive potentials, whereas the electron donating substituents increase the electron density on the azo group thus facilitating the oxidation process. This can be considered a proof that oxidation occurs most probably on the azo moiety.

It was found interesting to correlate E_{CT} with the absolute difference between $E_{1/2}^{OX}$ and $E_{1/2}^{R}$ ($\Delta E_{1/2}$). This runs in good harmony with the general correlation reported in literature for other types of molecules[35,36]. Analysis of our experimental data of $\Delta E_{1/2}$ and E_{CT} by the least square sequential simpler method results in the following equation with an excellent correlation coefficient of 0.986:

$$\Delta E_{1/2} = -0.169\ (\pm 0.013) + 0.198\ (\pm 0.033)\ E_{CT}\ .$$

Adopting the experimentally determined values of E_{CT} and $\Delta E_{1/2}$, a trail was also made to compute the coulomb repulsion integral (J_{12}) according to the equation[37]:

$$E_{CT} = \Delta E_{1/2} - J_{12}\ .$$

It should be appointed here that this method of estimation of the parameter J_{12} is much more direct and easier than the known complicated method based on semi-empirical molecular orbital theories. The values $E_{1/2}^{R}$, $E_{1/2}^{OX}$, *EA*, *IP*, E_{CT} and J_{12} are compiled in Table II.

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