

paraLocalization Energy and Polarographic HalfWave Potentials of Polynuclear Hydrocarbons

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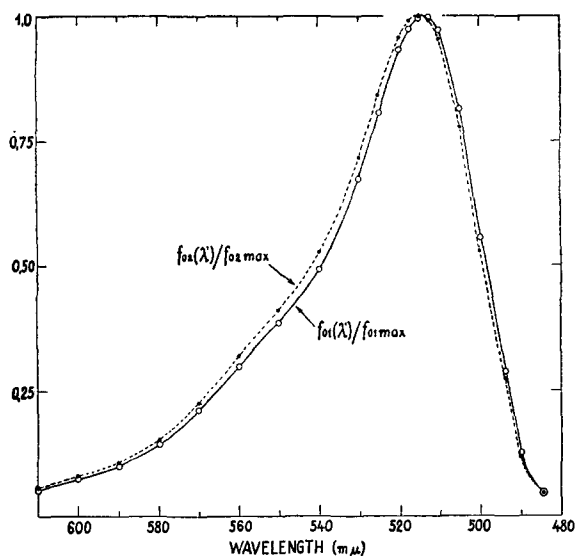


FIG. 2.

circular cross section $R^2\pi$ which beam is perpendicular to the front surface of the cuvette and a parallel light beam of small cross section, emitted in the opposite direction to that of the excitation is observed from the luminescence radiation, then for the fluorescence intensity³ $I_{\lambda'}$ on the middle of the irradiated surface of the cell

$$I_{\lambda'} = \frac{\rho}{4\pi\eta^2} E_{\lambda 0} \cdot l k_{\lambda} f(\lambda') \frac{1 - \exp[-(k_{\lambda} + k_{\lambda'})l]}{(k_{\lambda} + k_{\lambda'})l} (1 + \kappa), \quad (1)$$

where $E_{\lambda 0}$ represents the intensity⁴ of the exciting light on the front surface, n the refractive index, k_{λ} and $k_{\lambda'}$ the absorption coefficients of the solution for the wavelengths of the excitation and observation, respectively, η the quantum yield, and ρ a factor taking into account the reflection losses. κ representing the intensity ratio of the secondary and primary fluorescence light is

$$\kappa = \int_0^{\infty} \eta(\lambda'') f(\lambda'') M d\lambda'',$$

$$M = \frac{\gamma}{2\alpha\beta} [1 - \exp(-(\alpha + \beta))]^{-1} \{ (\alpha + \beta) [1 - \exp(-\alpha)] \times [1 - \exp(-\beta)] [Ei(-m\gamma) - Ei(-\gamma)] + (\alpha + \beta) G(-\gamma) - \alpha G(-\beta - \gamma) - \beta G(-\alpha - \gamma) + [(\alpha + \beta) G(-\gamma) - \alpha G(\beta - \gamma) - \beta G(\alpha - \gamma)] \exp(-(\alpha + \beta)) \}, \quad (2)$$

with abbreviations $\alpha = lk_{\lambda}$, $\beta = lk_{\lambda'}$, $\gamma = lk_{\lambda''}$, $m = R/l$ and $G(x) = Ei(x) - \ln|x|$. It was assumed that the total reflection at the limiting surfaces is eliminated. The influence of the tertiary, quaternary, etc., fluorescences may also be approximately considered when in (1), instead of $1 + \kappa$, $1/(1 - \kappa)$ is written. From Eq. (1) the true spectrum $f(\lambda')$ required can approximately be determined if κ is calculated with the approximation $f_0(\lambda')$ of $f(\lambda')$ derived from (1) with $\kappa = 0$ and the value of κ obtained in this manner is substituted into (1).

In order to investigate experimentally the spectral effect of secondary fluorescence for a given case, the $I_{\lambda'}$ -s of an alkaline fluorescein solution of two different thicknesses were directly compared with a photoelectric equipment with a good approximation of the experimental conditions mentioned. (Data: $l_1 = 0.10$ cm; $l_2 = 1.00$ cm; $k_{\lambda} = k_{436} \text{ m}\mu = 4.73$.) If the secondary fluorescence had no effect (i.e., for $\kappa = 0$), then, according to (1), we should obtain for $I_{\lambda'1}$ and $I_{\lambda'2}$ measured at the two layer thicknesses:

$$\left(\frac{I_2}{I_1}\right)^* = \frac{I_{\lambda'2}}{I_{\lambda'1}} \frac{1 - \exp[-(k_{\lambda} + k_{\lambda'})l_1]}{1 - \exp[-(k_{\lambda} + k_{\lambda'})l_2]} = 1,$$

whereas the measurements give the curve illustrated in Fig. 1. However, taking into account the effect of the secondary, tertiary,

etc., fluorescences the expression $(I_2/I_1)^{**} \equiv (I_2/I_1)^* \cdot 1 - \kappa_2/1 - \kappa_1$ must be equal to 1 and this is actually fulfilled with good approximation (Fig. 1). For the calculations was used a spectral distribution of η corresponding to the investigations of Vavilov,⁵ with $\eta_{\text{max}} = 0.74$. The spectra $f_{01}(\lambda')$ and $f_{02}(\lambda')$ obtained in the case of the two thicknesses taking only the reabsorption into account differ according to Fig. 2 perceptibly from each other. If, however, the effect of the secondary fluorescence is taken into account the two spectra practically coincide, and therefore this spectrum (which is almost identical with $f_{01}(\lambda')$ on Fig. 2) can be considered as the true spectrum required.

A more detailed report will be published in *Acta Physica Hungarica*.

¹ Th. Förster, *Fluoreszenz Organischer Verbindungen* (Vandenhoeck und Ruprecht, Göttingen, 1951), pp. 35-42.

² M. D. Galanin, *Trudy Fiz. Inst. Akad. Nauk. S.S.S.R. Fiz. Inst. im. P. N. Lebedeva* 5, 339 (1950).

³ Measured in (number of photons)/(cm² sec steradian mμ).

⁴ Measured in (number of photons)/(cm² sec).

⁵ S. I. Vavilov, *Z. Physik* 44, 539 (1927).

para-Localization Energy and Polarographic Half-Wave Potentials of Polynuclear Hydrocarbons

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It has recently been shown by Basu¹ that the difference in the π -electron energy between the oxidized and the reduced form of an aromatic compound may be effectively correlated with the oxidation-reduction potential of the system. In fact it is the π -electron energy difference between the parent compound and the transition complex which is the important variable portion of the free-energy change for the reaction, and as the geometric structure of the product and the transition complex is about the same the proposed calculation is justified. In this connection we may go a step further and state that the π -electron energy difference is the deciding factor in the reduction of aromatic compounds in general. Let us take the case of reduction at the dropping mercury electrode. It has been shown by Wawzonek and Laitinen² that a number of polynuclear hydrocarbons are electroreducible in 75% dioxan solution which contains 0.175 M tetrabutyl ammonium iodide. The polarogram consists of one sharp wave corresponding to a two-electron addition step. The process also resembles the reduction of these compounds by alkali metals and alcohol. Since it is an established fact that in the latter case the hydrogen addition takes place at *para*-positions of the compound, we may assume that in the polarographic reduction, the two-electron, two-proton addition process takes place at the *para*-positions too. The π -electron energy difference in the reduction will therefore be the same as the formation of adduct involving the localization of two electrons at *para*-positions to form two σ C-C bonds. This energy quantity has been defined as *para*-localization energy (P) and calculated for a number of aromatic compounds by Brown³ using the LCAO MO method and by Basu⁴ using the FE MO method. So if the views we are advocating be justified then the

TABLE I.

Compounds	Positions	$P(-\beta)^a$	E_1 vs S.C.E. ^b
Naphthalene	1:4	4.00	2.50
Anthracene	9:10	3.31	1.94
Phenanthrene	1:4	3.77	2.46
1:2-Benzanthracene	5:10	3.41	2.03
1:2:5:6-Dibenzanthracene	5:10	3.51	2.07
Biphenyl	1:4	4.38	2.70

^a See reference 3.

^b See reference 2.

para-localization energy should be directly proportional to the polarographic half-wave potential, which in turn is related to the free-energy change of the process. The values of half-wave potentials and *para*-localization energies of a number of aromatic hydrocarbons are summarized in Table I. When E_1 is plotted against $P(-\beta)$ a good straight line is obtained. It has been shown by Hoihtink *et al.*⁵ that if these compounds are reduced in 75% and 95% dioxan solution in absence of tetrabutyl ammonium iodide, the polarogram is much more complex, and waves corresponding to the one- and two-electron addition steps are obtained. If however, for the same solvent, E_1 for two-electron addition steps is plotted against $P(-\beta)$ a straight line is always obtained, although the absolute values of E_1 varies slightly from solvent to solvent. This is not unexpected since, as the reactions are ionic they should depend on the dielectric constant of the medium. The one-electron addition step is much more complicated, and its exact chemical consequences are not known. If this point could be established then the E_1 for the step may be correlated with the energy necessary to localize the electron at a particular position, which has been termed localization energy by Dewar.⁶

¹ Basu, *Trans. Faraday Soc.* **52**, 6 (1956).

² Wawzonek and Laitinen, *J. Am. Chem. Soc.* **64**, 2365 (1942).

³ Brown, *J. Chem. Soc.* 1950, 691.

⁴ Basu, *J. Chem. Phys.* **23**, 1548 (1955).

⁵ Hoihtink *et al.* *Rec. trav. chim.* **73**, 355 (1954).

⁶ Dewar, *J. Am. Chem. Soc.* **74**, 3359 (1952).

Vibrational Spectra of Diazines

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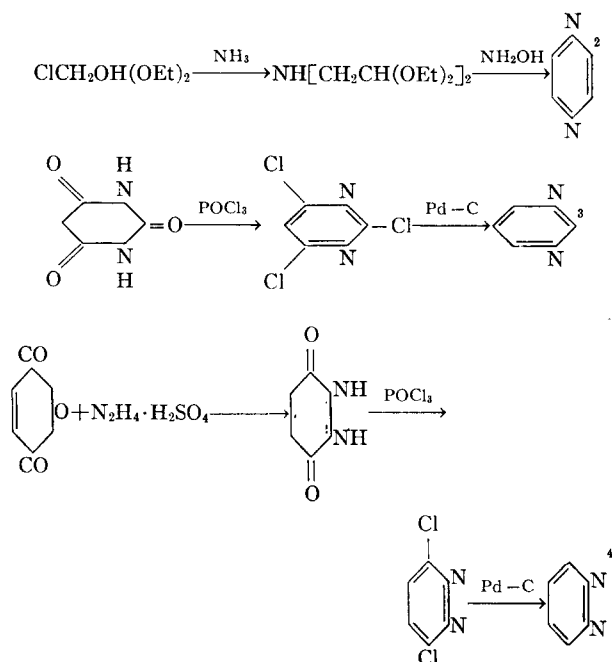
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ALTHOUGH there are many investigations which deal with the electronic spectra of diazine molecules, little attention has been paid to their vibrational spectra. The only available datum is of the infrared spectra observed by Barnes *et al.*¹ and literature which deals with the Raman spectra is scanty at the present time. Recently, we have been engaged in the study of ultraviolet absorption spectra of diazine vapors. In connection with it, observations of the Raman and infrared spectra of these molecules have been carried out and the results are reported in the present letter.

The samples used here were prepared by one of us (T.K.) according to the following procedures:



The diazines obtained were purified by repeating distillations just prior to taking the spectra. The Raman spectra were obtained in the liquid state with exposures ranging from 5 to 15 hr, using a 2-prism spectrograph constructed in this laboratory.⁵ Qualitative depolarization measurements of strong Raman lines were made by using a Wollaston prism.⁶ The infrared spectra were obtained for the liquid and the Nujol paste with a Perkin Elmer model 112 spectrometer equipped with a NaCl prism.

The observed Raman and infrared frequencies and the depolarization data of Raman lines are summarized in Table I.

For pyrazine molecule, it is found that there are no identical frequencies that occur both in the Raman and infrared spectra. This satisfies the rule of mutual exclusion of Raman and infrared

TABLE I.

Pyrazine			Pyrimidine			Pyridazine		
Raman (liquid)	Depol.	Infrared (Nujol paste)	Raman (liquid)	Depol.	Infrared (liquid)	Raman (liquid)	Depol.	Infrared (liquid)
601 (1)			400 (0)					
680 (0)			629 (1)		667 w			665 s
703 (3)	dp		682 (3)	dp	678 m			
753 (0)					719 s			759 s
		784 s						
		795 s			795 w			
					812 s			
925 (1)			990 (5)	p	992 s	964		964 s
1015 (5)	p	1019 s			1025 w			
		1064 s	1056 (4)	p	1055 m	1063		1063 s
		1110 s	1074 (4)	p	1071 s			
		1127 s	1135 (3)	dp	1139 m			1131 w
		1149 s						
		1176 m			1160 s	1159		1160 w
1233 (4)	p	1414 s	1228 (3)		1226 s	1283		1284 s
		1490 s			1400 s			1414 s
1523 (3)	dp				1470 s			1449 s
1577 (3)	p?		1567 (4)		1565 s			1565 s
					1617 m			
3054 (5)	p		3050 (5)	p	3044 s	3059		3062 s
			3122		3125 s			3140 m