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The Relation between the Electronic Spectra and the Oxidation and Reduction Potentials of Benzenoid Hydrocarbons

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Synopsis. It was shown that the ${}^1L_a$ band of benzenoid hydrocarbons is in a linear relation to $(E^{red}_{1/2}-E^{oxd}_{1/2})$ value led from the half-wave reduction and oxidation potentials. The theoretical background and the binding conditions of the application of this relation were clearly given.

In an earlier paper[1)] we have theoretically shown the linear relation of the electronic spectra to the non-aqueous oxidation and reduction potentials of organic substances. That is, we wrote:[1)]

$$E^{red}_{1/2} - E^{oxd}_{1/2} = k_1 \cdot {}^1E^{UV}_{HO\to LV} + k_2 \tag{1}$$

where $E^{red}_{1/2}$ and $E^{oxd}_{1/2}$ are the half-wave potentials (in volts) of the non-aqueous reduction and oxidation respectively. The ${}^1E^{UV}_{HO\to LV}$ is the singlet electronic transition energy, in which the contribution from the highest occupied molecular orbital (HOMO) to the lowest vacant MO (LVMO) is predominant. The absolute value of the k_1 constant equal 1 theoretically under suitable conditions[1)] when an electron volt is taken as the energy unit for ${}^1E^{UV}_{HO\to LV}$. It should be noticed that Eq. (1) is an extension of Eq. (2) (given below), which also satisfies the experimental results quite well.[1)] Here, ε_{LV} and ε_{HO} are the energy at the LVMO and the HOMO respectively:

$$E^{red}_{1/2} - E^{oxd}_{1/2} = k_1(\varepsilon_{LV} - \varepsilon_{HO}) + k_3 \tag{2}$$

In order to derive Eq. (1) from Eq. (2), however, there are necessary some binding conditions regarding the treatment of electronic transitions from the viewpoint of the electronic structures of molecules;[1)] these conditions limit the applicability of Eq. (1) to the ${}^1E^{UV}_{HO\to LV}$ transition. Previously Pysh and Yang,[2)] and Peover[3)] reported the linear relation of the p-band of benzenoid alternant hydrocarbons (AH) to the value of $E^{red}_{1/2}-E^{oxd}_{1/2}$. However, there have been no detailed discussions of this physical meaning from the standpoint of electronic structures, *i.e.*, the nature of applied electronic transitions and the value of k_1 in Eq. (1) and (2). Note particularly that the k_2 value in Eq. (1) should depend not only on solvation energy of the cation or anion radical,[3)] generated by electrolysis, but also on the electronic-state terms.[1)]

Although Eqs. (1) and (2) can well explain the ${}^1L_a$ band of the electronic spectra of heterocyclic amine *N*-oxide,[1)] it seems to be theoretically important to check whether or not these equations can be applied to other systems, especially to AH substances. This is because the AH's are the fundamental substances for testing theoretical treatments concerning molecular physics. The ${}^1L_a$ band (*p*-band)[4)] reported in the literature is adopted as the value of ${}^1E^{UV}_{HO\to LV}$. Actually, the energies at the ${}^1L_a$ and ${}^1L_b$ (α-band) bands are cited from Clar's book,[5)] in which the main vibrational peaks at the ${}^1L_a$ and ${}^1L_b$ bands are given. Either the vibrational peak appearing on the longest-wavelength side or that showing the strongest intensity was selected. However, the derived conclusion has the same, regardless of the choice. In addition, Peover *et al.*[6)] reported the value of $E^{red}_{1/2}$ and $E^{oxd}_{1/2}$ of AH's measured in acetonitrile. As the molecular orbital energies we have used those calculated by Koutecký,[7)] adopting the variable β method within the PPP π electron technique, since his puropse was to interpret the polarographic reduction and oxidation potentials. All the experimental and theoretical data mentioned above are collected in Table 1.

Figure 1 gives the linear relation of the $(E^{red}_{1/2}-E^{oxd}_{1/2})$ values against the ${}^1L_a$ band energies, the relation of Eq. (1) being well satisfied. The slope of $|k_1|=0.941$ is quite reasonable from the theoretical point of view.[1)] Also, note that the good linear relation of Eq. (2), $(E^{red}_{1/2}-E^{oxd}_{1/2}=-0.815\ (\varepsilon_{LV}-\varepsilon_{HO})+1.701)$, also holds with the standard deviation of $\sigma=\pm 0.071$ volt. We have also checked the constancy of the electron repulsion and CI terms,[1)] given by $(J_{ho\cdot lv}-2K_{ho\cdot lv}-{}^1E_{CI})$, for the ${}^1L_a$ band of the compounds listed in Table 1. Our results[8)] calculated using the PPP approximation with a constant β value (−2.37 eV) indicate that $(J_{ho\cdot lv}-2K_{ho\cdot lv})$ and $(J_{ho\cdot lv}-2K_{ho\cdot lv}-{}^1E_{CI})$ are within the maximum variations of 2.25±0.30 and 2.35±0.35 ev respectively in all the compounds except for benzene,[4)] for which they are 2.92 and 3.33 eV respectively. It is possible to put these values as a constant, this condition being required for deriving Eq. (1).[1)] In the case of ${}^1L_b$ band, however, each point is considerably scattered from the relation of Eq (1). Since the effect of the configuration interaction on the ${}^1L_b$ band seems to be much larger than that on the ${}^1L_a$ band,[9)] the above result is reasonably expected. It is now clear, from the facts thus far presented, that Eqs. (1) and (2) can be safely applied also to the benzenoid AH's, and that, conversely speaking, the treatment of Eqs. (1) and (2) is reasonable.

Next, let us consider some other points. For the AH's this equation: I_p (ionization potential)$+E_A$ (electron affinity)=constant is well known.[4b)] In other words, when Koopmans' theorem[4b,10)] is applied, the ε_{HO} (or ε_{LV}) can be expressed in terms of the ε_{LV} (or ε_{HO}) on the basis of the above relation. Therefore, using Eq. (2), $(E^{red}_{1/2}-E^{oxd}_{1/2})$ can be linearly expressed by either the ε_{LV} or the ε_{HO}. Since $(E^{red}_{1/2}-E^{oxd}_{1/2})$ is proportional to ${}^1E^{UV}_{HO\to LV}$ (Eq. (1)),[1)] we can conclude that the ε_{LV} or ε_{HO}, thus, $E^{red}_{1/2}$ or $E^{oxd}_{1/2}$, is also in a linear relation only to the ${}^1L_a$ band for the AH substances.[11)] That is, this relation is easily given by this equation: $E^{red}_{1/2}$ (or $-E^{oxd}_{1/2}$)$=(k_1/2){}^1E^{UV}_{ho\to lv}+k_4$ (new constant). This kind of plot employing the data given in Table 1

Table 1. Various benzenoid hydrocarbons, with their half-wave oxidation and reduction potentials (V *vs.* SCE), SCF-MO energies at LVMO and HOMO, and observed positions (eV) at ^1L_a (*p*) and ^1L_b (α) bands

Compound	Oxidation and reduction potentials[a)]		SCFMO energies[b)]		Observed band positions[c)]	
	$E_{1/2}^{\text{oxd}}$	$E_{1/2}^{\text{red}}$	ε_{HO}	ε_{LV}	^1L_a-band (*p*)	^1L_b-band (α)
Benzene	2.38[6)d)]	(−3.53)[e)]	−10.661	−1.339	6.205[f)]	4.761[f)]
Naphthalene	1.65	−2.63	−9.700	−2.300	4.350[f)]	4.174[f)]
Anthracene	1.19	−2.07	−9.086	−2.914	3.310[f)]	—
1,2-Benzanthracene	1.33	−2.11	−9.169	−2.831	3.491[g)]	3.219[g)]
1,2,5,6-Dibenzanthracene	1.40	−2.12	—	—	3.542[h)]	3.147[h)]
Pyrene	1.25	−2.19	−9.092	−2.908	3.718[f)]	3.337[f)]
1,2-Benzpyrene	1.34	−2.22	−9.200	−2.800	3.741[i)]	3.563[i)]
3,4-Benzpyrene	1.10	−1.95	−8.857	−3.143	3.225[i)]	3.076[i)]
3,4,9,10-Dibenzpyrene	1.17	−1.90	—	—	3.160[g)]	2.863[g)]
Perylene	1.04	−1.73	−8.808	−3.192	2.857[f)]	3.674[f)]

a) Taken from the Ref. 6 unless otherwise noted. These values were measured *vs.* SCE in CH_3CN containing 0.1 N. Et_4NClO_4. Generally speaking $E_{1/2}^{\text{red}}$ values correspond to those of a good reversible one-electron reduction wave at a dropping mercury electrode.[6)] The values of $E_{1/2}^{\text{oxd}}$ are also for the reversible one-electron oxidation at a rotating platinum electrode,[6)] except for anthracene, 1,2-benzanthracene, and 1,2-benzpyrene where the reversibility is not so good as an overall electrode reaction.[6)] In turn the reversibility on the $E_{1/2}^{\text{oxd}}$ values of benzene, naphthalene, and perylene is not clearly given in the cited literature.[6)] b) See Ref. 7. The relation of I_p+E_A = constant is well known for AH's[4b),c)] (see text). ε_{LV} was obtained from ε_{HO} by adopting the 12.0 eV for the constant.[7)] c) Taken from the Ref. 5 (see text). d) This is the value[6)] corrected *vs.* SCE on the data reported by H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957), where the potential was measured in CH_3CN *vs.* Ag electrode. e) This value was estimated from the extrapolation of the linear relation between $E_{1/2}^{\text{red}}$ and ε_{LV} in a series of benzenoid AH's.[6,7)] f) Obtained in CH_3OH-C_2H_5OH mixture. g) Obtained in benzene. For comparative purpose the 300 cm^{-1} was added to the value of the recorded ^1L_a band alone for correcting to that in ethanol. See E. Clar, *Spectrochim. Acta*, **4**, 116 (1950). h) Obtained in dioxane. i) Obtained in ethanol.

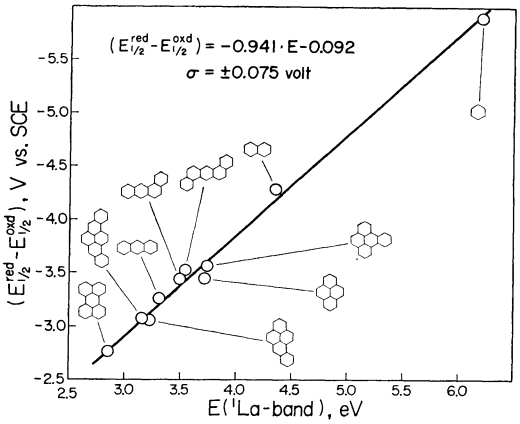

Fig. 1. The relationship between the observed values of ^1L_a band and $(E_{1/2}^{\text{red}}-E_{1/2}^{\text{oxd}})$ for benzenoid hydrocarbons.

also leads to a good linear relation with the slopes of −0.536 and −0.405 for the $E_{1/2}^{\text{red}}$ and $E_{1/2}^{\text{oxd}}$ plottings respectively. These absolute values of the slope are near the theoretical one, 0.5.

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