Correlation of the Lowest HMO Transition Energies with the Electronic Absorption Frequencies of Some Organic Dyestuffs: s-Cyanines & Merocyanines

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The long wavelength electronic absorption frequencies of some symmetrical cyanines, their aza-analogues, and merocyanines have been correlated with the transition energies calculated by Hückel molecular orbital theory. By systematically varying the carbon-nitrogen and carbon-oxygen coulomb integrals an optimum correlation is obtained with parameter values h_N (alkylated ring nitrogen) $= 0.5$, h_N (exocyclic) $= 0.3$, and $h_0 = 1$. With a judicious construction of the parent carbanion from which the dyes are supposed to be derived, the final regression lines, with high correlation coefficients and low standard deviations, conform unexpectedly well to the simple theory.

THE Hückel molecular orbital (HMO) method has been successfully used to correlate the electronic absorption spectra of many unsaturated hydrocarbons with lowest HMO transition energies[1]. But relatively little work of this type has been done on systems containing heteroatoms[2]. HMO calculations on organic molecules in which heteroatoms are present often tend to become crude[3] and quite justifiably the aim in such studies has been to examine the compatibility of a chosen model with an observed property rather than on correct numerical agreement with experiment.

Of primary importance in the HMO technique are the values chosen for the parameters, since they determine the outcome and therefore represent the essentials of the model conceived[4]. Earlier studies on systems containing heteroatoms reveal that the theoretical method sometimes leads to absurd results[4] and hence purely empirical values of parameters such as coulomb and resonance integrals is adopted.

The title dyes are supposed to be derived from a parent carbanion[3a]. With a knowledge of the energies and the coefficients of Hückel pi-orbitals for the highest occupied nonbonding orbital (HOMO) and the lowest unoccupied antibonding orbital (LUMO), it is possible to calculate the frequency of the lowest energy absorption band with the help of Eq. (1)[5]

$$\nu = \Delta E_i + \sum_{\mu}(C^2\mu_0 - C^2\mu_1)h_\mu\beta \qquad ...(1)$$

ΔE_1 is the energy difference between the nonbonding ψ_0(HOMO) and the lowest antibonding ψ_1 (LUMO) of the corresponding carbanion in β units, $C\mu_0$ and $C\mu_1$'s are the atomic orbital coefficients of the atom μ that has undergone replacement; in the HOMO and LUMO respectively.

The atomic orbital coefficients for the μth atom in the xth MO can be calculated by Eq. (2) for a straight chain n-atomic alternant hydrocarbon

$$C\mu x = \sqrt{\frac{2}{n+1}} \sin\frac{\mu x\pi}{n+1} \qquad ...(2)$$

and since all the parent carbanions are odd-atom systems with even number of pi-electrons, the HMO transition energy ΔE_1 for the transition between the HOMO and LUMO ($\Psi_0 \rightarrow \Psi_1$) is given by Eq.(3)

$$\Delta E_1 = -2\beta \sin\frac{\pi}{n+1} \qquad ...(3)$$

where n is the number of pi-centres.

It is at once obvious that in order to solve Eqs. (1), (2) and (3) one must know, in addition to the values of the heteroatom parameters h_x, the correct precursor carbanion so as to ascertain the number of pi-centres (n), the total number of pi-electrons, N (for Ψ_0 and Ψ_1) and the position of substitution (μ's). In the following treatment we present a scheme for the formulation of the parent carbanion within the purview of the classical resonance formalism which, along with the suggested values for the heteroatom parameters, yields results that are in excellent agreement with experiment.

Choice of the Carbanion

Dyes derived from thiazole derivatives — In dyes with sulphur containing nuclei it is assumed that sulphur acts as a resonance transmitter by extending its vacant d-orbital and thus behaves as a vinyl group[6].

In constructing the parent carbanion, we have therefore, considered a vinyl group in place of sulphur. The carbanion corresponding to the monomethine cyanine (I) would, therefore, be (Ia).

The central methine group in I now corresponds to the position-7 in the carbanion (Ia). In otherwards the cyanine (I) can now be considered as a derivative of Ia with the replacement of the carbon atoms 1 and 9 by nitrogen and its alpha-aza analogue (I, X=N) by the replacement of carbon atoms 1, 7 and 9 of Ia by nitrogen.
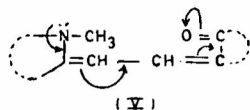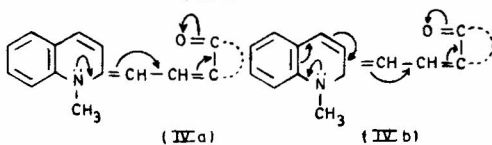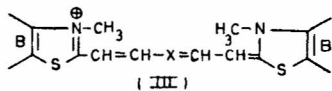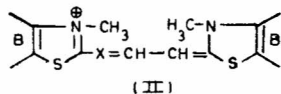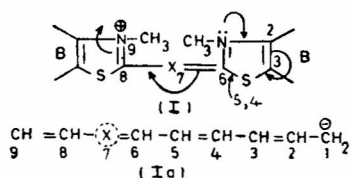
Since the system consists of 10 pi-electrons, the HOMO corresponds to Ψ_5 and the LUMO to Ψ'_6. In order to solve Eq. (1), we, therefore, need the following atomic orbital coefficients:

For the cyanine (I, X=CH): C_{51}, C_{59} and C_{61}, C_{69}

For the alpha-azacyanine (I, X=N): C_{51}, C_{57}, C_{59} and C_{61}, C_{67}, C_{69}

We can similarly construct the carbanions for the trimethinecyanine (II, X=CH), their alpha-aza analogues (II, X=N); pentamethinecyanines (III, X=CH) and their γ-aza analogues (III, X=N). The number of pi-centres (n), the number of pi-electrons (N) and the positions of substitution (μ's), on this basis can be calculated.

Merocyanines from quinoline-2 — For merocyanine dyes from quinoline-2, as in the previous calculations[6], the chromophoric chain is taken as the average of the following two structures (IVa and IVb).

The corresponding carbanion for the dimethine merocyanine (IV) will consist of 7 (for IVa) + 11 (for IVb)/2 = 9 carbon atoms. Similarly the number of pi-electrons will be 10 [(8+12)/2]. The required coefficients for a dimethinemerocyanines (IV) are, therefore, C_{51}, C_{59} and C_{61}, C_{69}. The number of pi-centres and the pi-electrons for the tetramethine

and hexamethine merocyanines are similarly calculated.

Other dyes — For all other dyes (benzoxazole-2, thiazoline-2, quinoline-4, etc.) the chromophoric chain is taken as the shortest conjugated chain lying between the two terminal heteroatoms as shown in structure (V).

Results and Discussion

Heteroatom parameters — A number of different coulomb parameter values, hx, for the alkylated ring nitrogen, the exocyclic nitrogen and the oxygen atoms were tried. For each set of parameters, the observed wave numbers (νkK) of the longest wavelength electronic absorption bands of all the dyes were correlated with transition energies expressed as Δm by means of least squares fit to the linear equation, $\nu = \Delta m\beta$. The plots of different correlation coefficients against the sum of coulomb parameters for each of the dye series showed a distinct maxima in the region, h_N (ring) $= 0.5$, h_N (exocyclic) $= 0.3$ and $h_0 = 1.0$. Hence these values were considered as constituting a self-consistent optimum set of values for this correlation[7] and they yielded regression lines characterized by high correlation coefficients (r) and low standard deviations (S). The various values of Δm calculated with h_N (ring) $= 0.5$, h_N (exocyclic) $= 0.3$ and $h_0 = 1.0$ are given in Table 1 for various values of n and N and different series of dyes. The regression line constants (β), correlation coefficients (r) and the standard deviations (S) for different series of dyes are described in Tables 2-4.

In the present treatment, similar geometries for the ground and excited states and a Frank-Condon transition have been assumed. With regard to electronic interactions and the spin-splitting, the purely empirical treatment of the parameters used in the present model reveals an interesting point. In the earlier MO calculations with hetero systems[1,8] large intercepts of the regression lines on the frequency axes were reported. The presence of these intercepts were attributed to the neglect of singlet-triplet splitting in the simple theory. The observed linear correlations were rationalized either in terms of a high degree of proportionality between the effects of configurational interaction, singlet-triplet splitting and the overall transition energy or as we have observed in our earlier calculations on unsymmetrical phosphocyanines and merophosphinines[9], by assuming that these factors are

TABLE 1 — n, N, ΔE_1 AND Δm VALUES OF DYES

n	N	E_1	$\nu = \Delta m\beta$		
			Cyanines	Azacyanines	Merocyanines
7	8	$-0.7654\ \beta$			$-0.7105\ \beta$
9	10	$-0.6180\ \beta$	$-0.5985\ \beta$ (I, X=CH)	$-0.5595\ \beta$ (I, X=N)	$-0.5893\ \beta$
11	12	$-0.5176\ \beta$	$-0.5064\ \beta$ (II, X=CH)	$-0.4814\ \beta$ (II, X=N)	$-0.5008\ \beta$
13	14	$-0.4430\ \beta$	$-0.4358\ \beta$ (III, X=CH)	$-0.4010\ \beta$ (III, X=N)	$-0.4322\ \beta$

TABLE 2 — REGRESSION LINE CONSTANTS (β), CORRELATION COEFFICIENT (*r*) AND STANDARD DEVIATION FOR CYANINES

Nature of B	λ (nm)		$-\beta$ (kK)	*r*	S (kK)
	II(X=CH)	III(X=CH)			
Benzothiazole	565	665	34·73	0·994	0·141
4-Phenylthiazole	565	660	34·86	0·998	0·057
α-Naphthothiazole	590	690	33·36	0·997	0·071
β-Naphthothiazole	590	690	33·36	0·997	0·071

TABLE 3 — REGRESSION LINE CONSTANTS (β), CORRELATION COEFFICIENTS AND STANDARD DEVIATIONS FOR AZACYANINES

Nature of B	λ (nm)			$-\beta$ (kK)	*r*	S (kK)
	I (X=N)	II (X=N)	III (X=N)			
Benzothiazole	400	465	555	44·75	0·998	0·058
4-Phenyl thiazole	390	455	555	45·52	0·994	0·206
α-Naphthothiazole	410	500	575	42·85	0·982	0·556
β-N aphthothiazole	410	496	580	42·85	0·985	0·453

TABLE 4 — REGRESSION LINE CONSTANTS, CORRELATION COEFFICIENTS AND STANDARD DEVIATIONS FOR MEROCYANINES

Nature of B	Nature of A	λ (nm)			$-\beta$ (kK)	*r*	S (kK)
		x=1	x=2	x=3			
Qhinoline-2	2-Benzyl thiothiazolone	549	650	—	30·82	0·997	0·078
do	2-Phenyloxazolone	540	640	—	31·32	0·996	0·094
do	Diphenylthiobarbituric acid	530	625	715	32·10	0·996	0·100
do	3-Phenylisooxazolone	525	626	728	32·03	0·994	0·152
do	1-Ph-3-Mepyrazolone	523	618	718	32·35	0·997	0·057
do	4-Hydroxycoumarin	508	592	—	33·57	0·995	0·120
Quinoline-4	2-Benzyl thiothiazolone	592	685	—	28·89	0·992	0·191
do	2-Phenyloxazolone	630	710	—	27·48	0·980	0·453
do	2-Phenylisooxazolone	586	685	795	29·07	0·997	0·063
do	1-Ph-3-Mepyrazolone	587	692	790	29·00	0·994	0·108
Benzoxazole-2	2-Benzylthiothiazole	490	590	—	28·74	0·992	0·071
do	1-Ph-3-Mepyrazolone	447	547	649	31·13	0·992	0·222
do	4-Hydroxycoumarin	465	550	627	30·89	0·984	0·471
Thiazoline-2	1-Ph-3-Mepyrazolone	426	522	—	32·79	0·992	0·233
do	Diphenylthiobarbituric acid	438	529	—	32·11	0·999	0·023
do	4-Hydroxycoumarin	439	525	—	32·18	0·996	0·127
do	5,6-Benzochroman-2,4-dione	440	535	—	31·18	0·996	0·127
do	3-Phenylthiohydantoin	444	505	—	32·56	0·970	0·944
do	7,8-Benzochroman-2,4-dione	448	537	—	31·49	0·988	0·085
do	3-Phenyl rhodanine	450	552	—	31·03	0·994	0·180

relatively unimportant in the case of dyes. In the present treatment, as also in the HMO treatment of the long wavelength electronic transitions in thiapyrylium salts[7], the excellent correlation of the optimum regression lines drawn by assuming a zero intercept, suggest that the large intercepts observed earlier could perhaps be more generally accommodated in the simple theory by a more appropriate choice of the empirical parameters.

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