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Electronic Energy Levels and Electron Donor Ability of γ-Pyrylocyanines and Their Heteroanalogues

A. D. Kachkovski, M. A. Kudinova, B. I. Shapiro,
N. A. Derevjanko, L. G. Kurkina
and A. I. Tolmachev

Institute of Organic Chemistry,
Academy of Sciences of the Ukrainian SSR,
252660 Kiev-94, Murmanskaja 5, USSR

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SUMMARY

Investigation by spectral and polarographic measurement as well as quantum-chemical calculations were carried out in order to estimate the relative and absolute positions of the frontier energy levels of γ-pyrylocyanines and their heteroanalogues. Correlations between the theoretical energy levels and the redox potentials as well as between the calculated energy gaps and the transition energies have been established. A new parameter—electron donor ability Φ_0*—has been used for the characterization of the relative position of the frontier MO.*

1. INTRODUCTION

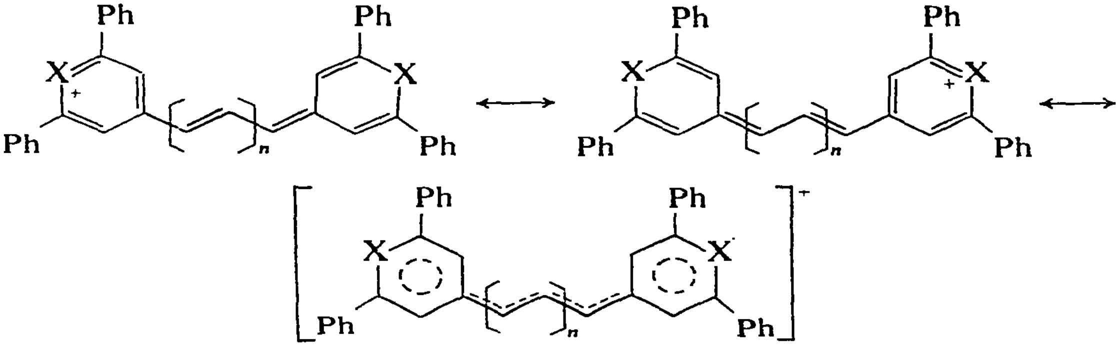
Many physical and chemical properties of dyes are determined by the spectrum of their electronic energy levels, especially frontier levels, i.e. the lowest vacant energy level (LUMO) and the highest occupied one (HOMO). For example, a knowledge of these values relative to the bottom of the conduction band and the top of the valence band of silver halide in the emulsion is very important for discussion of photographic effects of dyes.[1–4]

Information on the energy levels of the dye molecules may be obtained by experimental methods from measurements of their polarographic potentials, ionization potentials, energy of the electronic transitions, etc. However, with the progress of semi-empirical molecular orbital theory, it has become possible to obtain fruitful data on the electronic states of dyes by using computers. Relations between calculated energy levels and redox potentials of the typical cyanine dyes have been investigated by Tani and Kikuchi[5] as well as by other authors.[1-3]

We have applied a similar method for the investigation of γ-pyrylocyanines and their heteroanalogues.

2. MATERIALS

The formulae of cyanine dye cations studied in this paper are as follows:



I

We shall abbreviate these dyes as follows:

X	O	NMe	S	Se
Dye	O_n	N_n	S_n	Se_n

where n is the number of vinyl groups in the polymethine chain.

3. EXPERIMENTAL METHODS

3.1. Polarographic measurements

Polarographic curves of cyanine dyes **I** were measured for 5×10^{-5}–1×10^{-4} M solutions of dyes in acetonitrile; 0·1 M $NaClO_4$ was used as background electrolyte. The measurements of the redox half-wave potentials were carried out by means of a rotating glass–graphite disc electrode ($d = 3$ mm, $n = 1600$ rpm) and dropping mercury electrode ($m = 2{\cdot}3$ mg s^{-1}, $t = 3{\cdot}5$ s, $E = -0{\cdot}80$ V) relative to the saturated calomel electrode.

3.2. Quantum calculations

The electron energy level spectra of the type **I** dyes were calculated by means of the HMO (Hückel approximation molecular orbital) method[6] with the self-consistent field approximation (PPP method[7]). The atomic and bond parameters as well as the interatomic distances are listed in Table 1. The two-centre electron repulsion integrals of the electron interaction were calculated by the Mataga–Nishimoto formula.[8]

TABLE 1
Atomic and Bond Parameters

Atom, X	*Electron configuration*	h_X	η_{CX}	U_X (*eV*)	γ_{XX} (*eV*)	P_{CX} (Å)[a]	β_{CX} (*eV*)
C	trtrtr	0	1	−11·42	10·84	1·40	−2·318
NH	trtrtr^2	1·5	1	−23·13	12·98	1·40	−2·318
O	tr^{2}trtr^2	2	0·7	−27·17	14·58	1·40	−2·550
S	tr^{2}trtr^2	0·7	0·4	−20·27	9·80	1·70	−1·623
Se	tr^{2}trtr^2	0·6	0·35	−19·17	9·29	1·85	−1·391

[a] *l*: bond length.

PPP approximation: core integral, $U_\mu = \langle\mu|\hat{H}_{\text{core}}|\mu\rangle$; resonance integral $\beta_{\mu\nu} = \langle\mu|H_{\text{core}}|\nu\rangle$; one-centre integral of electron interaction, $\gamma_{\mu\mu} = (\mu\mu/\mu\mu)$.
HMO approximation: Coulomb integral, $\alpha_X = \alpha + h_X\beta$; resonance integral, $\beta_{CX} = \eta_{CX}\beta$.

Steric effects in dye molecules were taken into consideration. Phenyl groups are thought to be out of plane with respect to the rest of the molecule because of the steric hindrance between their hydrogen atoms and the heterocyclic ring. Evidence for these effects has been provided by PMR investigations.[9] According to these investigations, the angles between the phenyl groups and the heterocyclic ring are: $\theta \approx 0$–$10°$ (O_n), $\theta \approx 40°$ (S_n), $\theta \approx 40$–$50°$ (Se_n), $\theta \approx 60°$ (N_n). These steric effects were simulated by variation of the bond parameter: $\beta_{CPh} = \beta\cos\theta$.

4. RESULTS AND DISCUSSION

4.1. Relation of the electron excitation energy to the distance between the frontier MOs

In the visible part of the dye **I** spectra an intense absorption band is observed, with a regular red shift with longer polymethine chains.

According to the MO theory, the long-wave absorption band is assigned to the first electron transition from the highest occupied energy level (ε_o) to the lowest vacant one (ε_e). The excitation energy $E_{\max}$ is given by an energy gap between the frontier MOs in the case of the HMO method

$$E_{\max} = \varepsilon_e - \varepsilon_o \tag{1}$$

The observed excitation energies are plotted against the calculated ones in Fig. 1, showing the clear linear relationship between them.

A theoretical estimation of the first absorption band position was obtained by PPP calculations. The wave function of the excited state $|S_1\rangle$ was written as an expansion by singly excited configurations $|\Phi_i\rangle$

$$|S_1\rangle = \sum_i T_i|\Phi_i\rangle$$

We used 16 lowest configurations according to Fabian.[10] Results of absorption maximum calculations are listed in Table 2.

The correlation between calculated and observed data is shown from Table 2 to deteriorate with increasing chain length. In addition, the theoretical vinylene shift ($V_1 = \lambda_{n+1} - \lambda_n$) shows considerable alternation in the case of all vinylogous series of the dyes **I**. This alternation is thought to be caused by a change of dye class (type).[11] For $n = 0, 2$, dyes **I** are of class A. In this case the highest occupied MO is symmetrical relative to the centre of symmetry and the lowest vacant MO is unsymmetrical. For $n = 1, 3$, dyes **I** are of class B, in which case the symmetry of the frontier MO's is opposite to that of class A. Investigations of this effect will be discussed in later papers.

It is to be noted that theoretical double vinylene shift ($V_2 = \lambda_{n+2} - \lambda_n$, e.g. $\lambda_2 - \lambda_0$ and $\lambda_3 - \lambda_1$) gradually decreases. A decreasing vinylene shift is a common defect of the standard PPP method in the case of excited state calculations by means of sole singly excited configuration expansion.[10]

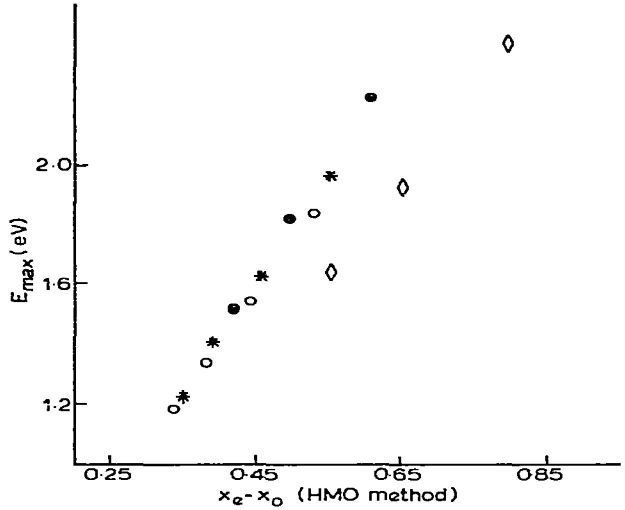


Fig. 1. The calculated E^{HMO} and the observed $E^{exp.}_{max.}$ excitation energies of dyes **I**: ●, O_n; *, S_n; ○, Se_n; ◇, N_n.

TABLE 2

Absorption Maxima of Dyes **I**

X	*n*	$\lambda^{theor.}_{max.}$ (*nm*)	V_1 (*nm*)	V_2 (*nm*)	λ^{exp}_{max} (*nm*)	V_1 (*nm*)	V_2 (*nm*)
NMe	0	489			512		
NMe	1	572	83		638	126	
NMe	2	677	105	188	748	110	236
NMe	3	755	78	183	—	—	—
O	0	504			552		
O	1	586	82		676	124	
O	2	696	110	192	798	122	246
O	3	774	78	188	—	—	—
S	0	525			627		
S	1	605	80		755	128	
S	2	716	111	191	879	124	252
S	3	794	78	189	1 000	121	245
Se	0	537			672		
Se	1	616	79		795	123	
Se	2	728	112	191	910	115	238
Se	3	805	77	189	1 035	125	240

$V_1 = \lambda_{n+1} - \lambda_n$; $V_2 = \lambda_{n+2} - \lambda_n$.

4.2. Redox potentials

Polarographic half-wave potentials give useful information about the energy levels of the dye molecules. For example, Tani *et al.* have reported in recent years that a linear relationship was observed between the HMO frontier levels and redox potentials for various typical cyanine dyes with quinoline, benzothiazole, benzoxazole and benzoselenazole end-groups.[5,12,13]

We used a similar method for the analysis of the γ-pyrylocyanines and their heteroanalogues. Results of the polarographic measurements are shown in Table 3.

TABLE 3
Redox Half-wave Potentials (versus SCE) of Dyes **I**

X	n	$E^{ox}_{1/2}$ (eV)	$E^{red}_{1/2}$ (eV)
NMe	0	0·55	−1·60
NMe	1	0·35	−1·25
O	0	1·20	−0·65
O	1	0·71	−0·59
O	2	0·55	−0·45
S	0	1·08	−0·46
S	1	0·65	−0·42
S	2	0·48	−0·30
S	3	0·30	−0·26
Se	0	1·06	−0·36
Se	1	0·71	−0·25
Se	2	0·59	−0·20
Se	3	0·53	−0·10

As has been indicated,[5,12,13] the reduction and oxidation potentials ($E^{red}_{1/2}$ and $E^{ox}_{1/2}$, respectively) of the conjugated molecules are related to the lowest vacant electronic energy level ε_e and the highest occupied one ε_o by following equations

$$E^{red}_{1/2} = -\varepsilon_e + C = -(\alpha + x_e\beta) + C \tag{2}$$

$$E^{ox}_{1/2} = -\varepsilon_o + C' = -(\alpha + x_o\beta) + C' \tag{3}$$

where x_e and x_o are the roots of secular equations for frontier MO, and α

and β are Coulomb and resonance integrals, respectively (in HMO approximation). As shown in Fig. 2, there is a satisfactory linear relationship between oxidation potentials and the highest occupied levels as well as a linear relationship between reduction potentials and the lowest vacant levels. The values of monomethine cyanine ($n = 0$) have been found to deviate a little from the straight lines. These discrepancies between redox potentials and MO energy are thought to indicate the existence of steric effects, which were not taken into consideration in the HMO calculations in the case of monomethine cyanine. Monomethine dye molecules are thought to be non-planar because of the steric hindrance between the heterocyclic rings. According to Tani[13,14] and Dyadyusha,[15] this perturbation in the chemical structure of dyes makes the lowest vacant level more stable and the highest occupied one less stable. The above conclusion is supported by the discrepancy between the calculated MO energy and observed values of redox potentials in the case of monomethine dyes.

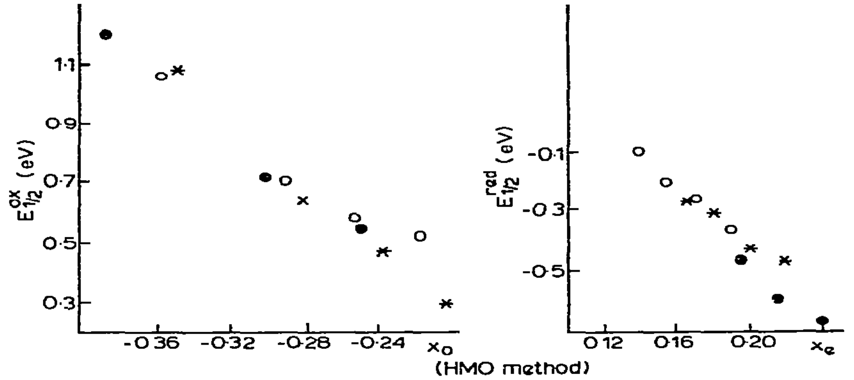


Fig. 2. Relation between redox potentials and HMO electronic energy levels of dyes I: ●, O_n; *, S_n; ○, Se_n.

In addition, account must be taken of solvent effects in the case of dyes with a long polymethine chain.

4.3. Electron donor ability of the dye end-groups

In this section we shall consider the important parameter of the dye end-groups—the electron donor ability, Φ_0.[16] This parameter characterizes quantitatively 'an additional double bond stabilization' or Brooker 'basicity'.[17] According to long dye theory,[16] Φ_0 determines the position of the frontier MO relative to the Fermi level (α) of the π-electrons. Electron donor ability can be theoretically calculated by the simplest formula

$$\tan\Phi_0 = -q_0/r_0 \tag{4}$$

where q_0 and r_0 are the first coefficients of the secular polynomials of the end-groups (Q) and their minors (R) (without the atom connected with the polymethine chain). Equation (4) can be used in the case of dyes of class A.[16] The invariant formula is more complicated

$$\Phi_0 = \tfrac{1}{2}\arccos\left(\frac{q_0^2 - r_0^2}{q_0^2 + r_0^2}\right) \tag{5}$$

The necessary coefficients of the secular polynomials (q_0 and r_0) can be easily obtained by graph theory.[16] The Sachs theorem enables the electron donor ability to be connected with the number of Kékulé structures and cycles as well as with the nature and positions of heteroatoms and heterobonds; thus, graph theory permits the parameter Φ_0 to be directly connected with information about the chemical structure of the dye end-groups.

In the HMO approximation, electron donor ability can be calculated by means of positions of the frontier energy levels

$$\Phi_0 = \lim_{n\to\infty}\left(\frac{\pi}{2}\cdot\frac{x_{e,n}}{x_{e,n} - x_{o,n}}\right) \tag{6}$$

where n is a number of vinyl groups in dyes **I**, x is the energy of MOs ($\varepsilon = \alpha + x\beta$), x_o is the highest occupied MO and x_e is the lowest vacant one.

Positions of the frontier MOs of dyes **I** are listed in Fig. 3. The absolute positions of the MOs are changed if the polymethine chain is lengthened but the change in the relative positions of the frontier energy levels relative to the Fermi level is small. For this reason, the relative positions of the frontier MOs of polymethine dyes can be characterized by the parameter

$$\Phi = \frac{\pi}{2}\cdot\frac{x_e}{x_e - x_o} \tag{7}$$

Calculated values of Φ of γ-pyrylocyanines and their heteroanalogues **I** with different numbers of vinyl groups (n) are listed in Table 4. For large values of n, the parameter Φ is approximately equal to Φ_0. Therefore,

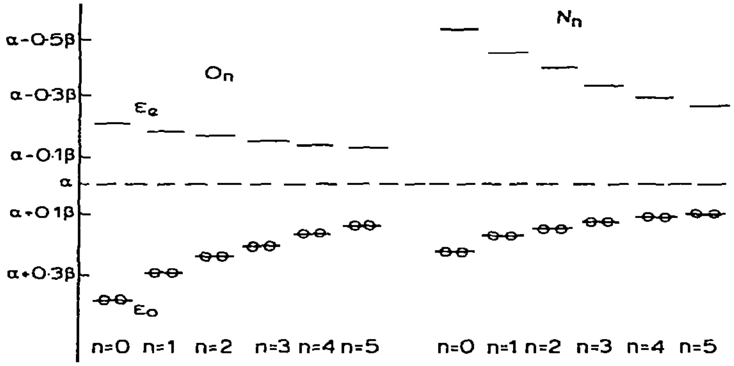


Fig. 3. The electronic energy levels of dyes I calculated by the HMO method; *n* is the number of vinyl groups in the polymethine chain.

electron donor ability may directly characterize a complete vinylogous series of polymethine dyes. The parameter Φ_0 is the quantitative characteristic of the basic property of the dye end-groups insofar as Φ_0 is to be correlated with the ionization potential and the electron affinity of the dyes.

The theoretical estimation of the basicity of the dyes I by means of the parameter Φ_0 is in good agreement with the experimental investigations of the basicity by means of the measurement of the deviations of the unsymmetrical dyes.[18]

The parameter Φ_0 can also be estimated experimentally. Substituting

TABLE 4
Electron donor ability of the dye end-groups[a]

n	$\Phi(O_n)$	$\Phi(S_n)$	$\Phi(Se_n)$	$\Phi(N_n)$
0	32·2	32·5	28·5	60·8
1	35·5	34·9	30·4	64·3
2	37·6	36·5	31·8	66·2
3	39·0	37·7	32·8	67·2
4	40·0	38·5	33·5	67·8
5	40·8	39·2	34·0	68·2
Φ_0	44·4	42·4	37·0	69·4

[a] All values in the table are given in degrees.

expressions (1)–(3) into eqn. (7), one obtains:

$$\Phi = \frac{\pi}{2} \cdot \frac{E_{1/2}^{\mathrm{red}} + C}{E_{\max}} \tag{8}$$

$$\frac{\pi}{2} - \Phi = \frac{\pi}{2} \cdot \frac{E_{1/2}^{\mathrm{ox}} + C'}{E_{\max}} \tag{9}$$

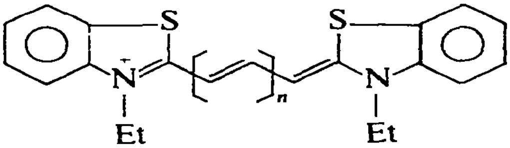
According to eqns (8) and (9), the reduction potentials (more exactly, the $E_{1/2}^{\mathrm{red}}$ values) of the dyes with weakly basic end-groups ($\Phi_0 < 45°$) should be smaller then those of the dyes with strongly basic end-groups ($\Phi_0 > 45°$), in the same region of dye absorption. On the other hand, the oxidation potentials of the weakly basic dyes should be greater. Experimental data are in harmony with this conclusion (Table 3).

Equations (8) and (9) may be rewritten in the form:

$$E_{1/2}^{\mathrm{red}} = \Phi \frac{2E_{\max}}{\pi} - C \tag{10}$$

$$E_{1/2}^{\mathrm{ox}} = \left(\frac{\pi}{2} - \Phi\right) \frac{2E_{\max}}{\pi} - C' \tag{11}$$

Values of redox potentials of the vinylogous series of thiacyanines



are plotted against those of $2E_{\max}/\pi$ in Fig. 4. The slope of the straight line gives an experimental value of the parameter $\Phi \approx 40°$. The theoretical HMO calculation gives $\Phi = 38°$ ($n = 5$, $\varepsilon_e = \alpha - 0{\cdot}1526\beta$, $\varepsilon_0 = \alpha + 0{\cdot}2059\beta$).[13]

The above results show, in principle, that the relationship between redox potentials and the transition energy can characterize the relative position of the frontier electron energy levels of these series of cyanine dyes.

Thus, the complex investigation by spectral and polarographic measurements as well as quantum-chemical calculations makes possible the estimation of the relative and absolute positions of the frontier energy levels of γ-pyrylocyanines and their heteroanalogues.

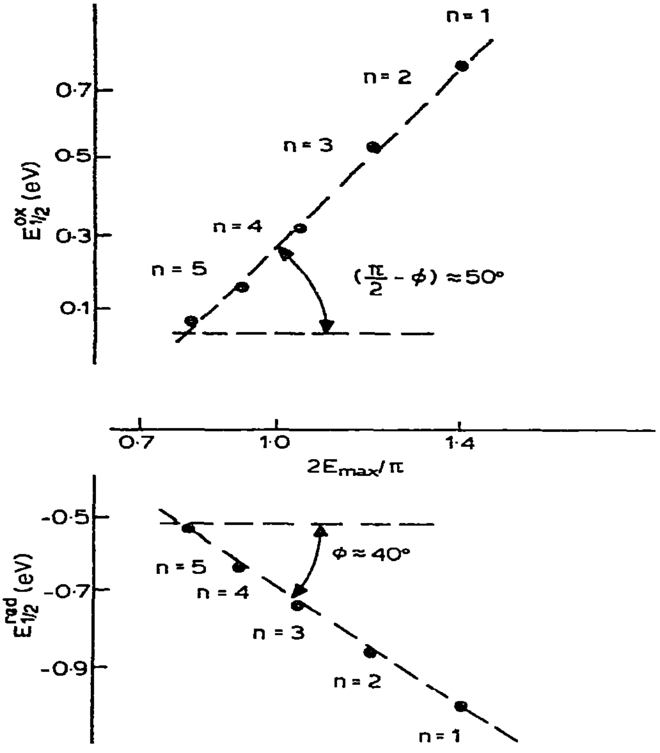


Fig. 4. Experimental estimation of the electron donor ability, Φ_0, of the benzothiazole end-groups: *n*, number of vinyl groups in the polymethine chain of thiacyanines.

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