SPECIFIC SEARCH FOR HETEROCYCLES FOR CYANINE DYES BY MEANS OF A COMPUTER

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A method for the selection by means of a computer of terminal heterocyclic groups for cyanine dyes that absorb over a predesignated spectral range is described. New monoazaheterocycles, the introduction of which into the compositions of cyanine dyes as terminal groups should ensure absorption in the near-IR region of the spectrum, are presented as examples.

Ever since the creation of the first synthetic dyes practical interests have time and time again dictated the necessary range of absorption of industrial samples of dyes. The demands of new technology have in recent years been responsible for the increased interest of chemists and physicists in cyanine dyes that absorb light in the near IR region due to electron transitions. The classical route to IR dyes consists in lengthening the polymethine chain between heterocyclic rings [1]. However, the sharp decrease in the stabilities of long-chain cyanines significantly reduces the prospects and practical value of this approach. A different route, viz., the search for new heterocycles which, upon introduction as terminal groups (G) into the compositions of polymethine dyes of the I type

$$[G^+-(CH{=}CH)_n-CH{=}G] \leftrightarrow [G=(CH-CH)_n{=}CH-G^+] \leftrightarrow [G-(CH\cdots CH)_n-CH-G]^+,$$

I

even when n is small, impart to them long-wave absorption without decreasing the stabilities of these compounds [2] seems more promising. Up until now the search for such heterocyclic rings has been carried out without any system, and the boundaries (950-1000 nm) of the absorption maxima of monomethylidyne cyanines (n = 0) and carbocyanines (n = 1) attained evidently still remain far from the possible limit. We set out to carry out a specific search for new promising heterocycles by means of a computer.

The search for heterocycles for dyes with a predesignated range of absorption presupposes a theoretical evaluation of the parameters of the electronic spectra and the chemical activities of the dyes constructed from them. Since monomethylidyne cyanines that are derivatives of two- and three-ring heterocycles contain no less than 20-30 carbon atoms and heteroatoms of the second or third period in their conjugated systems, we can speak only of semiempirical methods of calculation. However, the use of even the simplest such method, viz., the Hückel MO method, is fraught with colossal expenditures of computer time because of the enormous number of theoretically possible structures of the heterocycles. We therefore used the approximations developed for polymethine dyes, as well as well-known empirical principles. For example, the positions of the maxima of the long-wave bands for a vinylogous series of dyes I are described by the simple expression

$$\lambda_{\max,n}=V\cdot n+\lambda_0=V(n+L), \quad (1)$$

where V ≈ 100 nm is the so-called "vinylene shift," i.e., the shift of the absorption maximum when the polymethine chain is lengthened by one vinylene group, and $\lambda_0 = V \cdot L$ depends only on the structure of terminal groups G [3].

For a comparative evaluation of the stabilities of the dyes one can use the concept of the basicities of terminal groups G in them [4, 5]. The basicity characterizes the additional stabilization of the double bonds due to the terminal groups [5] and varies symbatically with the redox potentials [6] and pK_a [7] in series of dyes.

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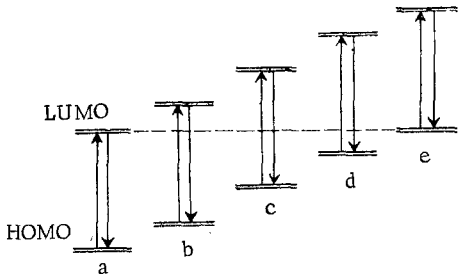


Fig. 1

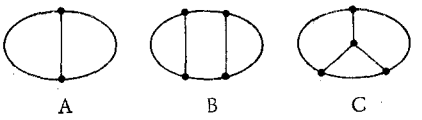


Fig. 2

Fig. 1. Arrangement of the boundary MO (HOMO and LUMO) of cyanines as a function of their electron-donor characters Φ_0: a) $\Phi_0 = 0°$; b) $0° < \Phi_0 < 45°$; c) $\Phi_0 = 45°$; d) $45° < \Phi_0 < 90°$; e) $\Phi_0 = 90°$. The Fermi level for the 2p electron is designated by a dash line.

Fig. 2. Cubic graphs corresponding to two- and three-ring condensed systems.

Since for unsymmetrical cyanines the additivity of λ_{max} is retained only if the basicities of terminal groups G differ little [4, 5], we will restrict ourselves to an examination of only symmetrical dyes in the search for new promising heterocycles for them.

In the present research the effective lengths L and electron-donor characters Φ_0 served as characteristics of the heterocycles when these heterocycles are included as terminal groups G in the compositions of dyes I [3, 8]. It is apparent from formula (1) that the effective length determines the position of the absorption maximum of a monomethylidyne dye with a given terminal group G in vinylene-shift units. The effective length should not be identified with the geometrical dimensions of the dye molecules. Parameter L shows only the number (not necessarily integral) of vinylene groups that the simple polymethine chain should contain in order that the maximum of its first absorption band may be found in the same region of the spectrum as the maximum of the band of a dye with a given terminal group.

The second parameter, viz., electron-donor character Φ_0, is a quantitative evaluation of the basicity of the terminal groups in the dyes [8, 9]. It characterizes the position of the boundary MO relative to the energy level of the unbonded 2p electron of the carbon atom of the polymethine chain (Fig. 1); the donor-acceptor properties of a dye with a given terminal group G can be judged from its magnitude. Dyes with small and large values of the Φ_0 parameter should display an increased tendency to redox reactions, and solutions of such dyes will be unstable. Those dyes for which the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) are situated symmetrically relative to the Fermi level (Fig. 1c) should be the most stable for a given width of the energy slit, i.e., for a predesignated absorption range.

Within the approximation of extremely long dyes [3, 8], the L and Φ_0 parameters are calculated theoretically in terms of the minor coefficients of secular polynomials for the G rings ($Q = q_0 + q_1x + \ldots$) and residues ($R = r_0 + r_1x + \ldots$) without the atom bonded to the polymethine chain

$$L = \frac{2q_1r_0 - 2q_0r_1 + q_0^2}{q_0^2 + r_0^2}, \tag{2}$$

$$\Phi_0 = \frac{1}{2}\arccos\left[(q_0^2 - r_0^2)/(q_0^2 + r_0^2)\right] \tag{3}$$

Under the assumption that dyes I have a stable closed shell, the interval of the change in Φ_0 is limited: $0 \leqslant \Phi_0 \leqslant \pi/2$ [8].

The value of the L parameter calculated from formula (2) may differ appreciably from the analogous parameter λ_0/V obtained in calculations within the Hückel MO approximation, since L is an asymptotic value; however, the results of the calculations coincide in the case of sufficient lengthening of the polymethine chain [3].

In the nonautomated calculation of L and Φ_0, and in the theoretical analysis of their dependence on the structure of terminal groups G, it is expedient to calculate the necessary

coefficients of the Q and R polynomials by means of the theory of graphs and, in particular, by means of the Sachs theorem [9-11]. However, in the case of calculation with a computer it is more convenient to proceed from the determinants of the Hückel Hamiltonians for the G rings and their minors: The free q_0 and r_0 terms are equal to the corresponding determinants, and the q_1 and r_1 coefficients are equal to the sums of the principal minors of order N — 1 (N is the order of the matrix of the Hamiltonian). We chose precisely this route. Its economy as compared with calculations by the Hückel MO method is due to the fact that the latter presupposes finding all of the coefficients of the secular polynomials or is equivalent to it, whereas in our case it is sufficient to find only the first two of them.

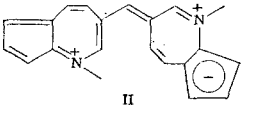
Let us also note that in this research we employed the standard Hückel Hamiltonian, in which the nonadjacent interactions are not taken into account, and the carbon atoms are assumed to be equivalent. The selection of this Hamiltonian is justified by the peculiarities of the chemical structures and electronic states of polymethine dyes and was discussed previously [3, 8, 9]. Under these assumptions, the Hamiltonian for hydrocarbons is proportional to the adjacency matrix [12], and the latter can be used directly for calculation of the L and Φ_0 parameters. Allowance for the heteroatoms requires only small corrections to the adjacency matrix, viz., the introduction of diagonal terms that are proportional to the Hückel approximation of the difference in the coulombic integrals of the heteroatom and the carbon atom in β units [$h = (\alpha_X - \alpha_C)/\beta$] and, if necessary, numerical corrections to the nondiagonal elements corresponding to the heterobonds and equal to the ratio of the resonance integrals $\eta = \beta_{CX}/\beta_{CC}$.

The described method, of course, shares all of the inadequacies of the Hückel MO and is, perhaps, inferior to it in accuracy in calculations of monomethylidyne- and carbocyanines [3]; on the other hand, the economy with respect to computer time turns out to be extremely significant (a factor of 20-50), not to mention how much computer time would be required when the PPP (Pariser—Parr—Pople) or CNDO (complete neglect of differential overlap) method is used. This becomes of decisive significance if the study of series of cyanine dyes that contain a large number of possible structures of the spectral properties of dyes is suitable, or it is sufficient to ascertain only the tendency of the change in these properties in the series. The use of more precise methods for the calculation of the electronic characteristics is expedient in the second stage, viz., in the analysis of the properties of selected promising structures.

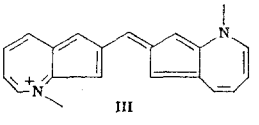
This method of calculation can be used to study terminal groups G with different heteroatoms, as well as carbocyclic G groups; this is achieved by using the corresponding computational parameters h and η.

In the present research as terminal groups G we tested all of the theoretically possible one-, two-, and three-ring structures with one nitrogen atom containing five-, six-, and seven-membered condensed rings. The selection of precisely these structures was dictated by two considerations: first, by the necessity for confining the investigated subjects within actually visible boundaries and, second, by the fact that precisely such heterocycles are included in the compositions of the overwhelming majority of cyanine dyes. The construction of all of the theoretically possible structures of terminal groups G (their numbers are presented in Table 1) and the calculation of the corresponding L and Φ_0 values were accomplished with a computer by means of the DYE program (FORTRAN-4), which was specially developed by us and was based on combinatorial and tabular methods.

A computer search for the structures of terminal groups G has the advantage that all of the theoretically possible cases are sorted out successively in this case, thereby excluding the loss of several structures and cases of repeated generation of the same heterocycles, which may occur when they are sorted out by hand. Nonclassical compounds for which one cannot write Kekule structures also will not be omitted in the case of successive sorting out. As an example, one may cite mesoionic dye II with rings of average basicity.



II



III

The generation of the structures of terminal groups G in mathematical terms is a task involving finding all of the possible nonequivalent markings of the apexes of a given graph, i.e., the G skeleton, with a certain number of markers. Examples of such graphs are

TABLE 1. Dependence of the Number of Theoretically Possible Condensed Carbocycles (l) and Heterocyclic Terminal Groups G (m) on the Number (k) of Five-, Six-, and Seven-Membered Rings from Which They are Composed

k	l	m
1	3	8
2	6	167
3	40	3280

presented in Fig. 2. The apexes of the graphs correspond to the nodal atoms of the skeleton; these may be C or N atoms. Carbon atoms or heteroatoms are distributed on the perimeter (the curves edges) until the necessary ring size is reached. For example, the skeletons of pentalene, indene, naphthalene, azulene, heptalene, etc. are produced from graph A, and the skeletons of fluorene, anthracene, phenanthrene, etc. and their heterocyclic analogs are produced from graph B.

In our case there are three types of markers: 1) skeletal carbon atoms that are considered to be indistinguishable (all except one), 2) the skeletal carbon atom from which the polymethine chain branches out, and 3) the heteroatom (nitrogen). During generation these markers "migrate" via the permitted positions of the heteroring skeletons themselves without a computer. One is easily convinced that there are three skeletons for one-ring G, six for two-ring G, and 40 for three-ring G with the ring sizes indicated above (Table 1). The adjacency matrixes (compendency matrixes) of the G skeletons served as the starting data. To arrange the markers we used the GOLF2E program, which was kindly furnished by its authors N. S. Zefirov and S. S. Trach (the mathematical substantiation of the algorithm is set forth in their paper [13]). The q_0, q_1, r_0, and r_1 coefficients for the calculation of L and Φ_0 were calculated by means of the standard computer procedures for expansion of the determinants that are built into the program. For the calculations we assumed that h_N = 1.5 and η_{CN} = 1.

It is convenient to present the results of the calculations in the form of diagrams. The effective lengths and electron-donor characters of some two-ring and three-ring heterocycles as terminal groups G are presented in Fig. 3 as an example. The diagrams are constructed as follows: The position of the nitrogen atom is designated on the contour of the heterocycle skeleton, and the λ_{max} values (in nanometers) are presented near each site of possible connection of the polymethine chain (all of the non-nodal carbon atoms) outside of the contour, whereas the Φ_0 values (in degrees) are presented inside the contour for dyes I and with a given heterocycle as the terminal group in a given position of connection of the polymethine chain. For example, if monomethylidyne dye III with connection of the polymethine chain in the 2 position is constructed from 4-azaazulene (Fig. 3a), it follows from the diagram that the theoretical wavelength of its first electron transition λ = 1492 nm, and electron-donor character $\Phi_0 = 34°$.

The results of the calculations show that the use of intuitively assumed principles in the search for needed dyes may lead to erroneous conclusions. For example, it is known that an increase in the number of rings in the terminal groups usually leads to a bathochromic shift of the absorption band [4]. However, it turns out that opposite situations are also possible. For example, dyes that contain the three-ring heterocycles depicted in Fig. 3b as terminal groups with connection of the polymethine chains in the indicated positions of the five- and seven-membered rings should absorb in the shorter-wave region of the spectrum than the analogous dyes with corresponding two-ring systems (Fig. 3a; the numbers compared are denoted identically in Fig. 3a and Fig. 3b).

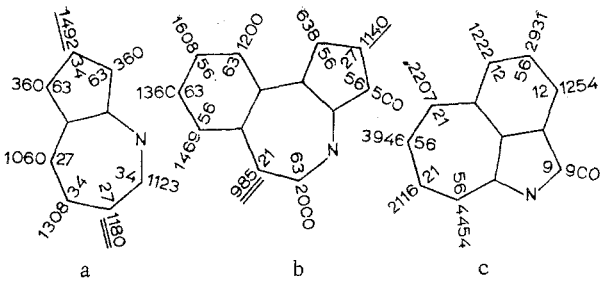


Fig. 3. Electron-donor characters Φ_0 (in degrees, inside the rings) and wavelengths (in nanometers) of the absorption maxima of monomethylidyne dyes constructed with given terminal groups in the indicated positions (for V = 100 nm) (see the text for the symbols).

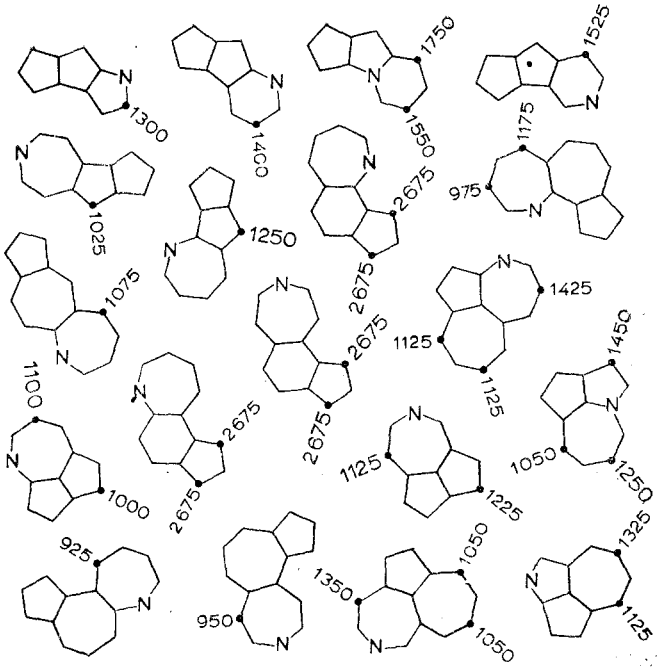


Fig. 4. List of all three-ring terminal groups G that have $\Phi_0 = 45 \pm 0.5°$ and $L > 9$ (the symbols are the same as those in Fig. 3).

A heteroring in which L takes on extremely large values even greater than 44 in a number of positions is presented in Fig. 3c. However, the results of calculations are reliable only for dyes that absorb in the near-IR region of the spectrum (on the order of 1300-1600 nm), since at higher values the energy of the electron transfer becomes commensurable with the energy of the ring vibrations. The large values of effective length L encountered therefore have significance only within the framework of a given model. They constitute evidence for quasi-degeneration of the boundary conditions, in which case our approximation is not sufficiently reliable.

Having a complete set of calculated structures at our disposal, it is not difficult to select heterocycles that will ensure a predesignated range of absorption and the necessary basicity. All of the possible heterocycles, the introduction of which into the compositions of polymethine dyes I as terminal groups G should ensure their highest stability ($\Phi_0 = 45°$) and absorption in the near-IR region of the spectrum, are presented in Fig. 4 as an illustration.

An analytical method for the selection of terminal groups D for a predesignated range of absorption determined by the L_{pre} value and with a predesignated electron-donor character Φ_{pre} is extremely convenient. Function (4) increases monotonically as its arguments L and Φ_0 approach the desired L_{pre} and Φ_{pre} parameters; the rate of the increase is regulated by the k coefficient.

For the selection process one must predesignate a minimal $f(L, \Phi_0)$ value, commencing with which terminal group G falls into the category of important groups from a practical point of view:

$$f(L, \Phi_0) = \cos^k(\Phi_0 - \Phi_{pre})/(L - L_{pre}) \quad (4)$$

It must be emphasized once again that this method does not guarantee high accuracy of the absolute values of the spectral parameters and gives the tendency rather than the order of their change and is therefore suitable primarily for the search for terminal groups G with extremal characteristics. Yet another limitation of the method described here should be noted: It does not reveal precisely which compound has a stable electron shell — the cation, the trication, the anion, etc. — and is therefore not applicable to the evaluation of the spectral properties of terminal groups G with two or more heteroatoms (both identical and different). However, these limitations are not substantial for a method in which the chief task is to narrow down a multiplicity of structures of the terminal groups for cyanine dyes with an optimal set of L and Φ_0 parameters and to uncover from them a small group of promising representatives for subsequent refinement of the indicated parameters by more accurate computational methods.

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