SYNTHESIS AND SPECTRAL PROPERTIES OF VINYLOGS OF HETERYLPOLYENES BASED ON PYRAN

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Vinylogs of unsymmetrical benzothiazole- and indolenine-substituted polyenes — pyran derivatives — were synthesized. Their absorption spectra reveal that the vinylene shift decreases with an increase in the length of the chromophore. The deviations of unsymmetrical heterylpolyenes prove to be negative and, for the same length of the chromophore, increase in absolute value with an increase in the difference in the electron-donor character of the terminal groups.

Vinylogous π-conjugated systems I with an open polymethine chain

$$\dot{G}_1-(\dot{C}\dot{H})_n-\dot{G}_2$$

I

where G are germinal groups of arbitrary structure, are known in the form of two series — polymethine and polyene — that differ substantially with respect to the character of the behavior of the first absorption band with lengthening of the polymethine chain by one vinylene group [1]. In the case of symmetrical polymethines (odd n) the vinylogous shift is virtually constant (V ≈ 100 nm), while equalization of the bond lengths and marked alternation of the charges in both the ground state and in the first excited state are characteristic for the polymethine chain. In the case of a vinylogous series of the polyene type one observes a regular decrease in the vinylogous shift V with an increase in the length of the chain, and the energy of the first transition tends to approach a certain limiting value [2]; this is explained by alternation of the double and single bonds. In the case of polymethines with unsymmetrical structures the electronic symmetry of the polymethine chain is disrupted, as a consequence of which the vinylene shifts decrease on passing to higher vinylogs [3]; the deviation from a constant value is greater, the greater the difference in the electron-donor properties of the terminal groups. The maximum of the long-wave band of unsymmetrical polymethines (λ_{unsym}) is shifted to the short-wave region as compared with the arithmetic mean of the maxima of symmetrical parent dyes λ_1 and λ_2. This phenomenon is called deviation [4, 5]; the magnitude of the deviation is determined from the expression

$$D = \frac{\lambda_1+\lambda_2}{2} - \lambda_{\text{unsym}} \qquad (1)$$

The deviation is proportional to the degree of electronic asymmetry of the dyes and is due to alternation of the bond lengths in the polymethine chain.

The parameter of electron-donor character Φ_0 [6] is used for the quantitative characterization of the terminal groups. The Φ_0 parameter ranges from 0° to 90°. The electronic asymmetry is conveniently evaluated by means of the difference in the electron-donor characters of the terminal groups: $\Delta\Phi_{12} = \Phi_{01} - \Phi_{02}$. It has been shown [7] that an increase in $\Delta\Phi_{12}$ in unsymmetrical polymethine dyes leads to an increase in alternation of the bond orders and a decrease in alternation of the charges in the chain. In this sort of approach it might be supposed that polyenes represent the extreme case of unsymmetrical polymethine dyes when the difference in electron-donor characters reaches the limiting value: $\Delta\Phi_{12} = 90°$.

However, in the case of unsymmetrical compounds of the polyene type disruption of the symmetry, on the other hand, should lead to equalization of the bond orders and an increase

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TABLE 1. Characteristics of Heterylpolyenes II-X

Compound	R		Empirical formula	mp, °C	λ_{max}, °C	$\varepsilon \cdot 10^{-4}$	D*, nm	V, nm	Yield, %
	X	Φ_0							
II [8]	CMe_2	33°	—	—	442	5,04	−18	—	—
III	—	—	$C_{32}H_{29}NO$	150...151	472	5,26	−8,5	30	12
IV	—	—	$C_{34}H_{31}NO$	168...170	476, 495	7,76, 7,11	−7,5**	23**	47
V [8]	S	48°	—	—	454	5,16	−24,5	—	—
VI	—	—	$C_{29}H_{23}NOS$	212...214	483,5	5,61	−10	29,5	63
VII	—	—	$C_{31}H_{25}NOS$	225...227	487,5, 506	7,05, 6,55	−13**	22,5**	42
VIII [8]	CH=CH	66°	—	—	456,5	5,01	−30,5	—	—
IX [8]	—	—	—	—	495	5,54	−36	38,5	—
X [8]	—	—	—	—	515,5	7,40	−32,5	20,5	—

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*The spectral data for the corresponding symmetrical heterylpolyenes were borrowed from [10, 11].

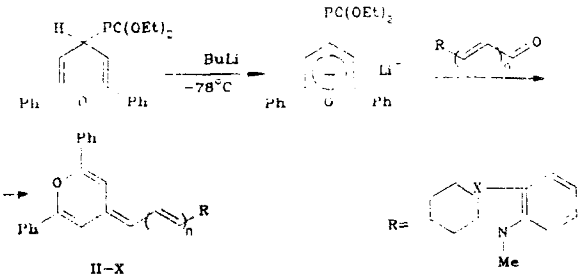
**Calculated from the long-wave inflection.

in alternation of the charges on the atoms, and these compounds, with respect to their electronic structures, therefore approach polymethine dyes.

We have previously synthesized [8] some unsymmetrical polyenes on the basis of pyran, the electron-donor character of which is 42° when it is used as the terminal residue of polymethine dyes, and investigated their absorption spectra. It was found that negative deviations, the absolute value of which is sensitive to a change in the nature of the second terminal group, are observed for such compounds.

The present research was devoted to the synthesis of higher vinylogs of unsymmetrical polyenes in which the weakly electron-donor indolenine ring and the moderately electron-donor benzothiazole ring were used as the second heteroresidue, as well as to the investigation of the character of the absorption spectra with lengthening of the conjugation chain and to a comparison of them with vinylogs of pyran-4-quino-2-polyenes.

Compounds III, IV, VI, and VII were obtained in the same way as polyenes II, V, and VIII-X [8] by the Wittig–Horner reaction between diethyl (2,6-diphenyl-4H-pyran-4-yl)phosphonate [9] and vinylogs of heterocyclic aldehydes:



X=CMe_2, II n=0, III n=1, IV n=2; X=S, V n=0, VI n=1, VII n=2; X=CH=CH, VIII n=0, IX n=1, X n=2

The spectral characteristics of unsymmetrical butadienes III and VI and hexatrienes IV and VII are presented in Table 1, in which data for our previously synthesized polyenes – pyran derivatives – are also presented for comparison.

The electronic absorption spectra of heterylpolyenes II-X have a complex structure with the manifestation of vibrational transitions. The spectra of the vinylogous series of heterylpolyenes V-VII are presented in Fig. 1. The distance between the individual bands and inflections is ~1200 cm^{-1}. The intensity of the short-wave band increases with an increase in the length of the polymethine chain, and for the last compound of the vinylogous series it becomes more intense than the long-wave band. The spectra of II-IV have a similar form.

It is apparent from the data in Table 1 and Fig. 1 that the vinylene shift in the series of polyenes II-X is 20-40 nm and that in all three vinylogous series its value decreases with lengthening of the polymethine chain. In the case of polyenes II-VI, when both terminal rings

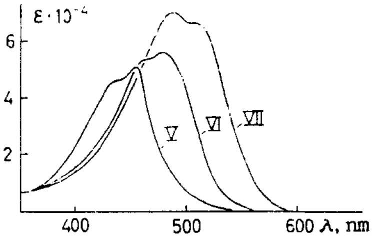


Fig. 1. Absorption spectra of heterylpolyenes V-VII.

have decreased electron-donor character, the decrease in the vinyl shift on passing to compounds with a longer polymethine chain is the smallest; in the case of heterylpolyenes VIII-X, where the quinoline residue has increased electron-donor character, the attenuation of the vinylene shift is, on the other hand, the greatest. This sort of behavior of the long-wave absorption band is also characteristic for the spectra of unsymmetrical polymethine dyes — pyrylium derivatives — for which one also observes a rapid decrease in the vinylene shift in the series of vinylogs, particularly if the second ring differs substantially in electron-donor character from the pyrylium residue [3].

The asymmetry of the electron distribution in the polyene chromophore can be characterized, as in the case of unsymmetrical polymethine dyes, by the deviation, which is calculated from formula (1). It is apparent from Table 1 that the deviations are negative for all of the unsymmetrical heterylpolyenes II-X, while their absolute values increase with an increase in the difference in the electron-donor characters of the rings vis-à-vis the same chain length. This fact can evidently be interpreted correctly if one assumes that alternation of the bonds is less pronounced in unsymmetrical polyenes than in symmetrical polyenes, in contrast to unsymmetrical polymethine dyes, for which an increase in the difference in the electron-donor characters of the terminal groups leads to an increase in alternation of the bonds and the development of positive deviations [3].

In the vinylogous series of polyenes II-V with rings with similar electron-donor character the absolute values of the deviations decrease somewhat on passing from heterylethylenes to butadiene-substituted compounds; a further increase in the length of the chromophore causes little change in the deviation. In the case of pyryloquinocyanines VIII-X, which have the greatest deviation, its change with an increase in the number of vinylene groups in the polymethine chain is relatively small.

EXPERIMENTAL

Vinylogs of Unsymmetrical Polyenes III, IV, VI, and VII. General Method [8]. A 6.7-ml (10 mmole) sample of a 1.5 M solution of n-butyllithium in hexane was added with stirring in an argon atmosphere to a cooled (to −78°C) solution of 3.69 g (10 mmole) of diethyl (2,6-diphenyl-4H-pyran-4-yl)phosphonate in 75 ml of dry tetrahydrofuran. The resulting dark-green solution was stirred for 10 min, after which the aldehyde (10 mmole) was added. The reaction mass was maintained at −78°C for 30 min, after which the temperature of the mixture was slowly brought up to room temperature, and the solution was evaporated in vacuo.

In the case of III and IV the residue remaining after evaporation was dissolved in benzene and purified with a column packed with aluminum oxide (elution with benzene). The solution was evaporated, and the residue was crystallized from isopropyl alcohol—toluene (1:1) (Table 1).

In the case of VI and VII 50 ml of methanol was added to the residue remaining after evaporation, and the mixture was heated to the boiling point and cooled. The resulting precipitate was removed by filtration, washed with methanol, dried, and crystallized from toluene (Table 1).

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REGIOSELECTIVITY AND STEREOSELECTIVITY OF ELECTROPHILIC QUATERNIZATION OF SUBSTITUTED 2-ALLYL(2-CYCLOHEXEN-1-YL)THIONICOTINIC ACIDS TO THIAZOLO[3,2-a]PYRIDINIUM SALTS

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The electrophilic quaternization of substituted 2-allyl(2-cyclohexen-1-yl)-thionicotinic acids proceeds regioselectively and stereoselectively as a trans process with the formation of salts of 4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo-[3,2-a]pyridinium acids. Trihalides of thiazolo[3,2-a]-pyridinium acids exist in equilibrium with their betaine form. The formation of betaines and reactions that proceed with a change in the anionic part of thiazolo[3,2-a]pyridinium salts have virtually no effect on the conformation of the heterocyclic cation.

The ability of heterocycles that contain an N=C—Y—CH—C=C fragment (Y = N, O, S, Se) to undergo quaternization under the influence of various electrophiles with the formation of rings makes it possible to obtain condensed heterocyclic systems in which pyridinium or pyrimidinium rings are annelated with imidazole, oxazole, thiazole, or selenazole rings and have a quaternary nitrogen atom as a nodal heteroatom [1-5]. The investigation of electrophilic quaternization makes it possible to isolate the general principles of the annelation of pyridines [1, 3, 4], pyrimidines [5], and 1,5-naphthyridines [6, 7] and to establish the stereostructures of quaternized condensed azines. The dependence of the three-dimensional structures of the reaction products on the structures of the starting compounds was established by comparison of the results of x-ray diffraction analysis with IR and PMR spectroscopic data.

We have observed that the electrophilic quaternization of hexahydrobenzothiazolo[3,2-a]-pyridinium salts proceeds stereoselectively as a trans process with the formation of cis-fused ring [7]. We assume that carbonium ions cannot act as intermediates in these reactions.

The aim of the present research was to develop methods for the synthesis of substituted 2-allyl(2-cyclohexen-1-yl)thionicotinic acids, to study the stereochemistry of their quaternization to thiazolo[3,2-a]pyridinium salts, and to establish the specific characteristics of the effect of the carboxy group on the structures and reactivities of the salts cited above.

2-Allyl(2-cyclohexen-1-yl)thionicotinic acids were obtained by alkylation of 6-methyl-3-carboxypyridine-2(1H)-thione with alkyl halides. Thus, the alkylation of I with alkyl halides IIa, b in DMF in the presence of an equimolar amount of a solution of KOH in water proceeds regioselectively exclusively at the sulfur atom with the formation of 2-alkenylthio-

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