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Abstract

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THE INFLUENCE OF TERMINAL SUBSTITUENTS IN DERIVATIVES OF 5-NITROFURYLPOLYENES ON THEIR ELECTRONIC SPECTRA

The question of the influence of various electron-acceptor and electron-donor substituents in derivatives of 5-nitrofuran of type Ia on the displacement of the absorption maxima of these substances in their electronic spectra was considered by us in previous communications ([1–3]).

$$\underset{(Ia)}{O_2N\text{—furan ring—}X} \qquad \underset{(IIa)}{O_2N\text{—furan ring—}(CH{=}CH)_n\text{—}X}$$

The present work is devoted to establishing the regularities in the transmission of the influence of terminal substituents X on light absorption in derivatives of 5-nitrofuran, if this influence is transmitted from the principal chromophore through a chain of conjugated bonds consisting of from one to four —CH=CH— groups. The compounds studied by us have structure IIa ($n = 0 \div 4$) and are listed in Table 1.

Table 1

Derivatives of 5-nitrofurylpolyenes
O_2N—furan ring—$(CH{=}CH)_n$—X

No.*	Terminal substituents X	a_1	a_2	k_1	k_2
I	$X = -COOC_2H_5$	8.7	4.0	2.4	1.6
II	$X = -CO-CH_3$	9.4	4.1	2.2	1.7
III	$X = -CHO$	10.1	4.9	1.9	0.7
IV	$X = -CH(OCOCH_3)_2$	9.6	4.3	2.1	1.3

No.*	Terminal substituents X	a_1	a_2	k_1	k_2
V	$X = -CH = N - NH - CO - NH_2$	14.5	7.0	1.1	1.0
VI	$X = -CH = N - NH - CS - NH_2$	14.6	8.2	0.9	0.8
VII	$X = -CH = N - NH - CO - CH_2 - CN$	13.2	7.9	1.4	0.8
VIII	$X = -CH = N - NHCO - C_5H_4N$	12.8	7.5	1.6	1.0
IX	$X = -CH = N - N - CH_2$ (cyclic imide fragment with CO, CO, NH)	12.5	7.2	1.4	1.0

Fig. 1

Figure 1: Fig. 1

No.*	Terminal substituents X	a_1	a_2	k_1	k_2
X	$X = -\mathrm{CH} = \mathrm{N} - \mathrm{N} - \mathrm{CO}$ (cyclic oxazolidone fragment with O, H_2C, CH_2)	12.2	7.0	1.5	1.4

* The numbers correspond to the numbers in Fig. 1.

For IIa, $X = \mathrm{CHO}$, the electronic spectra are also given in the work of Saikachi and Ogawa ([4]), devoted to the synthesis of similar compounds. As for the other substances presented in Table 1, they are described for the first time. The synthesis of these substances has been described in a number of communications ([3,5–7]).

The study of the optical properties of compounds containing polyene chains, as is known, has until very recently attracted the attention of investigators in connection with the development of a general theory of the color of organic substances. Quite some time ago, Hausser and coauthors ([8,9]) established the basic regularities in the displacement of absorption maxima in the electronic spectra of chiefly symmetric polyene systems. Subsequently, Lewis and Calvin ([10]), and in recent years Bayliss, Kuhn, Simpson, and others ([11–15]), made attempts to substantiate—and in some of the simplest cases also to calculate—both the absorption maximum itself and the magnitude of its displacement by means of the molecular-orbital method, proceeding from concepts of the quantum-mechanical oscillator and the potential well.

Fig. 1

The regularities in the electronic spectra of sharply asymmetric polyenes have been studied much less. They are considerably more difficult to calculate. Meanwhile, precisely such systems represent the most convenient models for studying one of the cardinal questions in the problem of the color of organic compounds, namely the question of the displacement of the absorption maximum under the influence of the interaction of the two previously mentioned factors: the terminal substituent X and the length of the "conducting" chain of atoms. In all the investigated derivatives of 5-nitrofurylpolyenes (IIa), naturally, a regular shift of the principal absorption maxima toward longer wavelengths is observed as the number of double bonds increases. This applies both to the two principal absorption maxima and to the third short-wavelength maximum in those cases where it can be observed.

We found that, with a sufficient degree of accuracy, the course of the displacement of the absorption maxima as a function of the number n obeys the law:

$$\lambda_{\max}^2 = a_i + k_i n, \tag{1}$$

where $\lambda_{\max}$ is the wavelength of the absorption maximum, n is the number of double bonds in the polyene chain, and a_i and k_i are constants characterizing each of the absorption maxima separately, as well as the type of substituent X,

which is in good agreement with the conclusions of Lewis and Calvin^(10):

$$\lambda_{\max}^2 = k' n, \tag{2}$$

where $\lambda_{\max}$ is the wavelength of the absorption maximum, n is the number of vinylidene groups in the chain, and k' is a constant equal to

$$k' = \frac{4\pi^2 cm}{k}.$$

Here m is the effective mass, k is the force constant of the harmonic oscillator; c is the speed of light.

The results of our measurements are presented in Fig. 1, from which it is evident that in most cases the straight line for the long-wavelength maximum has a steeper slope than the straight line for the short-wavelength maximum. Only in two cases is a parallel course of the straight lines observed. Thus, one may say that $k_1 \gg k_2 \gg k_3$.

It is interesting to note that k_1 is the larger, the smaller a_1 is, i.e., the farther into the ultraviolet region the long-wavelength absorption maximum is shifted. This means that, as the long-wavelength maximum is displaced toward the visible region, it as it were loses its mobility and reacts more weakly to a change in the length of the polyene chain. The regularity found is presented in Fig. 2. The relation between a_1 and k_1 proves to be almost linear.

Fig. 2

Fig. 2

Figure 2: Fig. 2

In the works of Lewis and Calvin^(10), Hausser and other authors^(8, 9), attention is paid only to the proportionality $\lambda^2_{\max} = k'n$. The physical content of the constant a_i is not considered. Only at Hausser' s suggestion is an empirical "color factor" introduced, dependent on the nature of the terminal functional groups. It is assumed that in the compounds considered by the authors mentioned the principal absorption of light is effected only by the polyene chain itself.

We have obtained absorption data for compounds in which $n = 0$. Absorption of light by such compounds corresponds to electronic transitions of interaction of both terminal functional groups, i.e., the nitrofuran nucleus and the substituent X, without participation of the conjugated system of vinylidene groups. It is found, however, that the points in Fig. 1 corresponding to $n = 0$ fit the straight line well. It follows from this that the principal absorption is effected by the nitrofuran group and the substituent X, and each vinylidene group introduced into the molecule merely shifts the absorption maximum by a definite amount.

The greater steepness of the course of the long-wavelength absorption maximum in the graphs of Fig. 1 indicates that it is more sensitive to displacements of the electron cloud of the polyene chain under the influence of the substituent at the end of the chain. The slope of the straight line itself, i.e., the constant k_1, depends strongly on the nature of the substituent X. As is evident from (2), the constant k_1 is inversely proportional to the coefficient of elasticity of the oscillator. In other words, an increase in the slope of the straight line indicates a "loosening" of the system.

These considerations indicate that the long-wavelength absorption maximum should be attributed chiefly to the substituent X, and the slope of the straight line, i.e., the constant k_1, may serve as a certain measure of the electron-donor or electron-acceptor properties of the substituent X.

As for the character and course of the displacement of the shorter-wavelength absorption maximum, the latter proves to be considerably more

is stable both in position and in degree of shift, and also depends comparatively less on the nature of the substituent and is less sensitive to changes in the length of the polyene chain. From this it may be concluded that this absorption maximum should be attributed mainly to electronic transitions in the nitrofuran chromophore itself.

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Note: Figure translations are in progress. See original paper for figures.