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CALCULATION OF THE ELECTRONIC SPECTRUM WITHIN THE CNDO/S (COMPLETE NEGLECT OF DIFFERENTIAL OVERLAP/S) APPROXIMATION AND CHARACTER OF THE LONG-WAVE ABSORPTION BAND OF 2-N-PYRIDINIA-1,3-INDANDIONE BETAINE

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The electronic spectrum of 2-N-pyridinia-1,3-indandione betaine was calculated by the MO LCAO method within the CNDO/S approximation with the Del Bene—Jaffe parametrization in order to refine the concepts regarding the character of the long-wave absorption band of this compound. It was established that the long-wave absorption band of this compound is due to an electron transition with charge transfer and has a vibrational structure.

The energy of the long-wave transition for 2-N-pyridinia-1,3-indandione betaine corresponds to the value expected on the basis of general concepts regarding intramolecular charge transfer [1]. A comparison of the dipole moments in the ground and first excited states [2] also constitutes evidence that the long-wave transition is a transition with charge transfer from the anionic to the cationic part of the betaine. The results of a calculation by the Hückel MO method [3] are in poor agreement with the experimental data as a consequence of the well-known inadequacies of this method [4].

The long-wave band in the electronic absorption spectrum of 2-N-pyridinia-1,3-indandione betaine in all solvents is clearly asymmetrical, whereas in the case of solutions in n-hexane one even observes a weakly expressed inflection (Fig. 1). The latter phenomenon may, in principle, also be due to the fact that the long-wave band arises as a consequence of the existence of two closely located electron transitions. In order to explain the experimental data, in the present research we calculated the 2-N-pyridinia-1,3-indandione betaine molecule

TABLE 1. Electron Transitions for 2-N-Pyridinia-1,3-indandione Betaine

No.	Calculated						Experimental	
	λ, nm	contribution of the orbital transitions	classification	polarization	oscillator force (f)	$\varepsilon^a = 5 \cdot 10^4 f$	λ, nm	ε^b
1	463	96% 41—42	$\pi-\pi^*$	X	0,383	19 150	431	33 490
2	360	86% 41—43	$\pi-\pi^*$	Y	0,003	150	365 pl.	3 060
3	334	93% 41—44	$\pi-\pi^*$	Y	0,023	1 150	340	1 800
4	317	86% 38—42	$n^- -\pi^*$	—	0,000	0,0	310	1 600
5	314	74% 38—44	$n^- -\pi^*$	—	0,000	0,0		
6	254	93% 39—42	$\pi-\pi^*$	X	0,013	650		
7	249	82% 40—42	$\pi-\pi^*$	Y	0,025	1 250		
8	248	71% 36—42	$\pi-\pi^*$	Y	0,23	11 500	243	32 790
9	241	69% 41—45	$\pi-\pi^*$	X	0,198	9 900		
10	228	71% 41—46	$\pi-\pi^*$	Y	0,29	14 500		
11	218	89% 39—45	$\pi-\pi^*$	X	0,03	1 500	—[c]	
12	212	72% 41—47	$\pi-\pi^*$	Y	0,013	650		
13	206	98% 39—43	$\pi-\pi^*$	Y	0,002	100		
14	205	43% 36—43	$\pi-\pi^*$	X	0,946	47 300		

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[a] This is the extinction coefficient. [b] Solution in n-hexane.
[c] The maximum of the band was not recorded.

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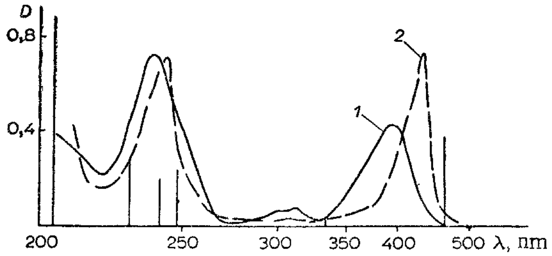

Fig. 1. Absorption spectra of 2-N-pyridinia-1,3-indandione betaine in ethanol and in n-hexane: 1) 96% ethanol, $c = 2.22 \cdot 10^{-5}$ mole/liter, $l = 1$ cm; 2) n-hexane, $c = 2.12 \cdot 10^{-5}$ mole/liter, $l = 1$ cm. The theoretical electron transitions are indicated by the vertical lines.

by the MO LCAO method within the CNDO/S (complete neglect of differential overlap/S) approximation with the Del Bene–Jaffe parametrization and made a simple analysis of the form of the long-wave absorption band in 11 solvents with different polarities and polarizabilities. In the calculation of the excited states we took into account 20 singly excited configurations. The scheme of the calculation was identical to that described in [5]. The geometry of the molecule was selected on the basis of an x-ray diffraction analysis of crystals of the monoclinic modification [6]. According to the data in [7], this approach leads to the best agreement with the experimental data in the case of calculation of the spectra and dipole moments of N-heterocycles and their methylated forms.

The energies of the electron transition obtained and their probabilities are presented in Table 1, while the distribution of the electron densities in the orbitals that participate in the first two electron transitions is presented in Fig. 2. Both of these transitions as the starting level have a higher occupied molecular orbital (41). This orbital is a π orbital, and the distribution of the electron density in it, in principle, differs little from that according to the Hückel MO method. The lower vacant orbital (42) and the next unfilled orbital are also π orbitals and have analogies in the calculation according to the Hückel MO method. However, their energy orientation is changed markedly. Both the 42 and 43 orbitals are localized on the pyridine residue, and only the 44 orbital, which is somewhat higher than the 43 orbital (0.358 eV), is localized on the phthaloyl part.

The calculated spectrum is in good agreement with the experimental spectrum. A difference between the theoretical and experimental spectra was noted only at 300-330 nm, in which region low-intensity absorption is observed in polar solvents. The latter may be due to elimination of the prohibition for the 4 and 5 transitions in accordance with Table 1. The long-wave band in solutions is shifted hypsochromically relative to the theoretically expected value. This is completely understandable, since the latter is characterized by pronounced negative solvatochromism, whereas the calculation was made for the isolated molecule. Using the dependence of the energy of this band on the function of the dielectric constant of the solvent [2], one can estimate the energy of this transition *in vacuo*. It turns out that this band is found at 460 nm, which is in good agreement with the calculation.

Unfortunately, the calculation does not expand our knowledge relative to the form of the long-wave band, the asymmetrical character of which may, in principle, also be associated with two closely located electron transitions.

The latter possibility must be excluded on the basis of an analysis of the experimental data. With this end in mind, we recorded and thoroughly analyzed the electronic absorption spectra of 2-N-pyridinia-1,3-indandione betaine in the visible region in 11 solvents with different polarities and polarizabilities.

If the long-wave band is due to two electron transitions that have opposite character, as follows from a calculation by the Hückel MO method, this band actually consists of two bands, which should be characterized by opposite solvatochromism. The transiton with charge transfer to the cationic part is associated with a decrease in the dipole moment of the ground state and should be characterized by negative solvatochromism, while the redistribu-

TABLE 2. Spectral Shift and Change in the Form of the Long-Wave Band When the Solvent is Changed

No.	Solvent	$\lambda_{\max}$, nm	Band half width, cm^{-1}	Asymmetric character[a]
1	96% ethanol	392	3840	1,45
2	Acetonitrile	398	3460	1,45
3	Acetone	402	3300	1,45
4	Pyridine	405	3250	1,56
5	Ethyl acetate	406	3170	1,48
6	Dioxane	409	3120	1,54
7	Chloroform	412	3000	1,58
8	Ethyl ether	414	2680	1,68
9	Triethylamine	420	2620	1,85
10	Carbon tetrachloride	427	2320	2,41
11	n-Hexane	431	2050	2,95

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[a] Ratio of the short-wave part of the half width of the band to the long-wave part.

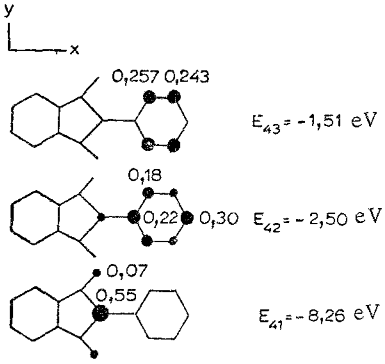

Fig. 2

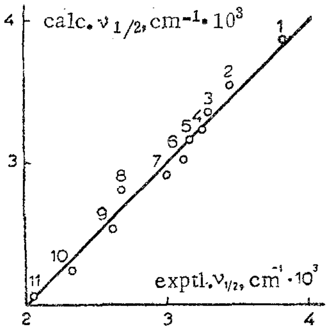

Fig. 3

Fig. 2. Distribution of the electron density in the orbitals that participate in the first two electron transitions.

Fig. 3. Interrelationship between the experimental and calculated half widths of the bands in various solvents. The numbering of the solvents corresponds to the numbers in Table 2.

tion of charge from the diketo to the phthaloyl part of the molecule is associated with an increase in the dipole moment of the ground state, and the transition should be characterized by positive solvatochromism. This means that, depending on the mutual orientation of these transitions in series of solvents with different polarities, one should observe either their separation or passage of the half width of the band through a minimum. The data in Table 2 provide evidence that this is not observed. An absolutely different principle, viz., an increase in the polarity of the solvent gives rise to a symbatic broadening of the band, is realized. Thus it should be assumed that the hypothesis that the long-wave absorption band is due to two electron transitions of opposite character (the intensities of which are of approximately the same order of magnitude) is not confirmed. The change in the asymmetrical character of the band is most readily explained by leveling of the vibron transitions. In fact, the asymmetrical character of the band on passing to a more polar solvent decreases rapidly, and commencing with dioxane it remains at a virtually constant value. If the latter assumption is correct, the broadening of the band should be subject to the same principles that follow from the concepts regarding the fluctuation mechanism of the effect of a solvent [8]. According to these concepts, an increase in the half width of the band and its spectral shift on passing from a vacuum to a solution are linked by the expression $\Delta\nu_{1/2} = (0.2\text{-}1.0)\Delta\nu$. Assuming that the maximum of the band in a vacuum is found at 460 nm (as follows from the solvatochromism of the band), it is easy to find that $\Delta\nu_{1/2} = 0.78\Delta\nu$ and that $\Delta\nu_{1/2}$ in a vacuum is $\sim$905 cm^{-1}. The $\Delta\ _{1/2}^{\mathrm{calc}}$ values obtained actually correlate well with the $\Delta\nu_{1/2}{}^{exp}$ values (Fig. 3), and this confirms the fact that this band is a vibronic band. Consequently, there is no basis for the assumption that the long-wave of 2-N-pyridinia-1,3-indandione betaine is due to two electron transitions. This band is actually a band with intramolecular charge transfer from the diketo to the pyridinium part and has a vibrational structure that becomes pronounced in solvents with low polarities.

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CONFORMATIONAL EQUILIBRIUM OF N-ACYL-1-METHYL-1,2,3,4-TETRAHYDROISOQUINOLINES

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The PMR spectra of N-acyl-1-methyl-1,2,3,4-tetrahydroisoquinolines were studied. The conformational parameters of retarded internal rotation about the partially double C—N bond were determined.

It is well known that amides, owing to the certain degree of double bond character of the C—N bond, exist in the form of two conformers, the ratio between which depends both on electronic and steric factors [1, 2].

To study the effect of steric factors on the conformational equilibrium of the amide group we synthesized N-acyl-1-methyl-1,2,3,4-tetrahydroisoquinolines (I). The choice of these substances for the investigation was due to the presence of an asymmetric center in the starting 1-methyl-1,2,3,4-tetrahydroisoquinoline (II), which makes it possible to subsequently ascertain the effect of the conformational composition on the optical activity of such amides.

The N-acyl-1-methyl-1,2,3,4-tetrahydroisoquinolines (Ia-f) were obtained by the action on amine II of the corresponding acid (for Ia), the anhydride (for Ib, c), or the acid chloride (for Id-f).

Doubling of the signals of the 1-H methylidyne proton, the protons of the 1-CH_3 group, and, in some cases, the protons of the acyl group, which is due to retarded internal rotation about the C—N bond, is observed in the PMR spectra of amides Ia-e at 25°C.

The character of the PMR spectrum is determined by the rate of exchange [3], which in turn depends on the temperature. Slow exchange (according to data from the PMR spectra) for Ia-e (R = H, CH_3, C_2H_5, n-C_3H_7, and i-C_3H_7) is observed at room temperature, while it was necessary to lower the temperature to −40°C for recording the PMR spectrum of both conformers of If (R = t-C_4H_9). Figure 1 illustrates the temperature dependence of the observed

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