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NATURE OF π-ELECTRONIC TRANSITIONS IN UV SPECTRA OF DEOXYVASICINONE AND ITS DERIVATIVES

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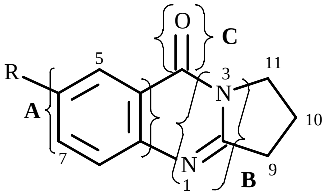
The principal types of electronic transitions in absorption spectra of deoxyvasicinone and its 6-amino- and 6-nitro-derivatives were determined by analyzing the electron-density distributions in excited states calculated using ZINDO/S.

Key words: quantum-chemical calculations, ZINDO/S method, UV spectra, deoxyvasicinone, 6-aminodeoxyvasicinone, 6-nitrodeoxyvasicinone.

Investigations of UV spectra and reactivity indices (RI) elucidated the effect of the nature of a substituent in the 6-position on the electronic structure of deoxyvasicinone (DOV, **1**) [1]. Studying the features of π-electronic transitions in UV spectra makes it possible to estimate electron-density distributions, which determine the reactivity factor and biological activity of organic compounds.

Representations of such electronic transitions, for which only certain parts (fragments) of the molecule are responsible, are used in spectroscopy of complicated conjugated molecules. In terms of molecular orbital (MO) theory, the localization of electronic excitation is evaluated using configuration analysis or data for the change of charge on atoms during excitation [2-5].

Therefore, the nature of π-electronic transitions in spectra of **1** and its 6-amino- (**2**) and 6-nitro-derivatives (**3**) was explained by calculating the degree of localization of MOs on separate fragments (A, B, and C) of **1-3** as sums of squares of coefficients for basis atomic orbitals (AO) of fragment atoms [6].



R = H (**1**); NH_2 (**2**); NO_2 (**3**)

Electronic transitions were described using changes of total fragment charges Δq_{φ_p}, e^- [7] in $S_0 \rightarrow S_k$ excitation and the excitation localization numbers (ELN), which indicate the relative contributions of molecule fragments to the overall molecular electron-density distribution ($L_{\varphi p}$, %) [3-6, 8-12]. These are defined as the ratio of the sum of the moduli of charge changes on fragment atoms to the analogous sum over all atoms of the molecule [6, 11].

Quantum-chemical calculations of electronic spectra (singlet transitions) were performed by the semi-empirical ZINDO/S method [13, 14] using full optimization of the molecular geometry by the PM3 approximation [15] and taking into account configuration interaction of six occupied and vacant MOs (73 singly excited configurations). Calculations were performed using the Hyperchem 6.0 (Hypercube Inc.) program set.

Tables 1-4 and Fig. 1 present the results of the calculations. Satisfactory agreement of the calculated and experimental values (Table 2 and Fig. 1) provide a basis for our proposed interpretation of the absorption spectra of **1-3**.

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TABLE 1. Principal Properties of MOs and Contributions of AOs to MOs of **1-3**

MO No.	MO energy, eV	MO type	Contributions of AOs to MOs, %			
			A	B	C	R
			Deoxyvasicinone (**1**)			
φ_4'	1.77	π*	52.0	13.4	32.8	-
φ_3'	1.23	π*	66.0	23.9	9.6	-
φ_2'	0.09	π*	36.3	50.2	11.4	-
φ_1'	-0.11	π*	58.6	14.7	25.8	-
φ_1	-8.26	π	66.6	25.2	6.7	-
φ_2	-9.14	π	90.0	0.8	7.3	-
φ_3	-9.99	n	6.4	8.0	83.5	-
φ_4	-10.29	π	23.6	52.6	15.5	-
φ_5	-10.54	n	19.0	74.4	2.3	-
			6-Aminodeoxyvasicinone (**2**)			
φ_4'	1.79	π*	51.2	13.4	33.3	0.8
φ_3'	1.26	π*	64.0	22.5	11.0	0.5
φ_2'	0.15	π*	35.9	53.4	7.1	0.7
φ_1'	-0.08	π*	58.8	9.8	29.6	-
φ_1	-7.80	π	64.4	17.4	4.5	-
φ_2	-9.17	π	90.2	1.2	6.2	10.4
φ_3	-9.95	n	14.7	44.5	26.7	9.8
φ_4	-9.97	n	8.2	14.0	73.0	1.2
φ_5	-10.51	n	18.7	74.2	2.1	-
			6-Nitrodeoxyvasicinone (**3**)			
φ_5'	1.16	π*	48.4	12.4	35.4	2.4
φ_4'	0.62	π*	57.1	27.0	9.8	3.5
φ_3'	-0.38	π*	30.6	50.8	4.3	12.4
φ_2'	-0.65	π*	61.3	6.5	29.6	2.0
φ_1'	-1.73	π*	13.4	4.1	-	73.0
φ_1	-8.92	π	59.0	28.6	7.6	3.4
φ_2	-9.84	π	88.4	0.8	7.3	-
φ_3	-10.49	n	5.8	7.3	82.9	0.8
φ_4	-10.82	π	23.9	49.5	14.0	1.7
φ_5	-10.88	n	-	-	-	98.5

The long-wavelength absorption band at 314.8 nm (Table 2 and Fig. 1) in the spectrum of **1** belongs to the $S_0 \rightarrow S_1$ transition ($n\pi^*$, 318.1 nm) localized on the carbonyl (C), which has a high ELN (L_C = 60.4%) on C=O (**1**, Table 3 and Fig. 1).

The absorption band at 303 nm (**1**, Table 2 and Fig. 1) corresponds to the calculated wavelength of the $S_0 \rightarrow S_2$ transition ($\pi\pi^*$, 296.6 nm). According to Table 3, a charge of 0.06 e^- is transferred during the $S_0 \rightarrow S_2$ transition from ring A and -0.07 e^- from ring B onto the carbonyl, i.e., a transition of the A + B → C type occurs. The dominating contribution of the A, B, and C fragments (L_A = 61.3%, L_B = 17.7%, and L_C = 21.0%) to the formation of the S_2 state confirms the conclusion stated above.

The strong absorption band at 265 nm (**1**, log ε = 4.04, Table 2) correlates with electronic transitions into S_3 ($\pi\pi^*$, 262.8 nm, f = 0.225) and S_4 ($n\pi^*$, 256.7 nm, f = 0.010) excited states, the energies of which are similar (Fig. 1).

The changes of total charges (Δq_{φ_p}, e^-) in $S_0 \rightarrow S_3$ (-0.20 e^-, A→B) and $S_0 \rightarrow S_4$ (-0.14 e^-, B→A) transitions and analysis of the ELN (L_A = 48.2%, L_B = 38.9%; L_A = 30.0%, L_B = 63.3%) lead to the conclusion that the band at 260-290 nm is due to interfragment charge transfers from A to B and from B to A. This corresponds to absorption of radiation by the A and B structural fragments.

TABLE 2. Properties of Electronic Transitions in **1-3**

$S_o \rightarrow S_k$ transition	Configuration contributions	Transition type	Calculation		Experiment	
			λ_{max}, nm	Oscillator strength (f)	λ_{max}, nm	log ε
Deoxyvasicinone (**1**)						
$S_0 \rightarrow S_1$	0.54 $\varphi_{3\rightarrow1'}$ 0.20 $\varphi_{3\rightarrow4'}$	n→π*	318.1	0.001	314.8	3.80
$S_0 \rightarrow S_2$	0.69 $\varphi_{1\rightarrow1'}$	π→π*	296.6	0.106	303.0	3.83
$S_0 \rightarrow S_3$	0.67 $\varphi_{1\rightarrow2'}$	π→π*	262.8	0.225	265.0	4.04
$S_0 \rightarrow S_4$	0.67 $\varphi_{5\rightarrow2''}$	n→π*	256.7	0.010		
6-Aminodeoxyvasicinone (**2**)						
$S_0 \rightarrow S_1$	0.52 $\varphi_{4\rightarrow1'}$	n→π*	318.1	0.002		
$S_0 \rightarrow S_2$	0.77 $\varphi_{1\rightarrow1'}$	π→π*	315.6	0.131	320_{infl}	
$S_0 \rightarrow S_3$	0.82 $\varphi_{1\rightarrow2'}$	π→π*	276.1	0.372	285.0	4.20
$S_0 \rightarrow S_4$	0.74 $\varphi_{5\rightarrow2'}$	n→π*	255.5	0.010		
6-Nitrodeoxyvasicinone (**3**)						
$S_0 \rightarrow S_1$	0.65 $\varphi_{3\rightarrow2'}$ 0.22 $\varphi_{3\rightarrow5'}$	n→π*	319.7	0.001		
$S_0 \rightarrow S_2$	0.92 $\varphi_{1\rightarrow1'}$	π→π*	316.6	0.495	324	4.08
$S_0 \rightarrow S_3$	0.46 $\varphi_{1\rightarrow2'}$ 0.37 $\varphi_{2\rightarrow1'}$	π→π*	300.1	0.015		

The $S_0 \rightarrow S_3$ (276.1 nm) and $S_0 \rightarrow S_4$ (255.5 nm) electronic transitions with an amino group present (**2**, Table 2) are, like for **1**, local excitations of fragments A and B, respectively (Table 3 and Fig. 1). Therefore, the band in the experimental spectrum of **2** at 260-290 nm is due to absorption of radiation by the A and B structural fragments (Table 3 and Fig. 1, **2**).

The bathochromic shifts and stronger absorptions (Table 2) in the experimental (λ_{exp} = 285 nm, log ε = 4.20) and theoretical (λ_{theor} = 276.7 nm, f = 0.372) spectra compared with spectra of **1** (λ_{exp} = 265 nm, log ε = 4.04; λ_{theor} = 262.8 nm, f = 0.225) are consistent with stronger donor properties of the heterocyclic system after introducing the amino group in the 6-position, mainly through excitation of the benzene of fragment A.

This agrees with the decrease in the energy of the $S_0 \rightarrow S_3$ transition (Fig. 1, E = 38046 cm^{-1}, **1** and E = 36218.7 cm^{-1}, **2**) and the increase of electron populations (Table 4) of the p_z AO of C-2 (0.939), C-5 (1.009), and C-7 (1.019) in **2** compared with **1**.

Based on the results of the calculations, the long-wavelength and strong band in the spectrum of **2** (λ_{exp} = 324 nm, log ε = 4.08, Tables 1-3 and Fig. 1) can be assigned to the $S_0 \rightarrow S_2$ electronic transition ($\pi\pi^*$, λ_{theor} = 316.6 nm, f = 0.495). The significant charge transfer ($\Sigma\Delta q$ = -0.57 e^-, Table 3) from fragments A and B into the nitro group and the predominant participation of fragments A and B and the nitro group (L_{AB} = 49.3%, L_R = 45.7%) in the overall molecular charge redistribution during the transition into the S_2 excited state enable the band to be assigned to charge transfer from the heterocyclic system into the nitro group. This conclusion is confirmed by the significant decrease in the electron populations of C-2 (0.895), C-5 (0.862), C-7 (0.903), N-1 (1.225), N-3 (1.651), and O (1.429) in **3** compared to **1** (Table 4).

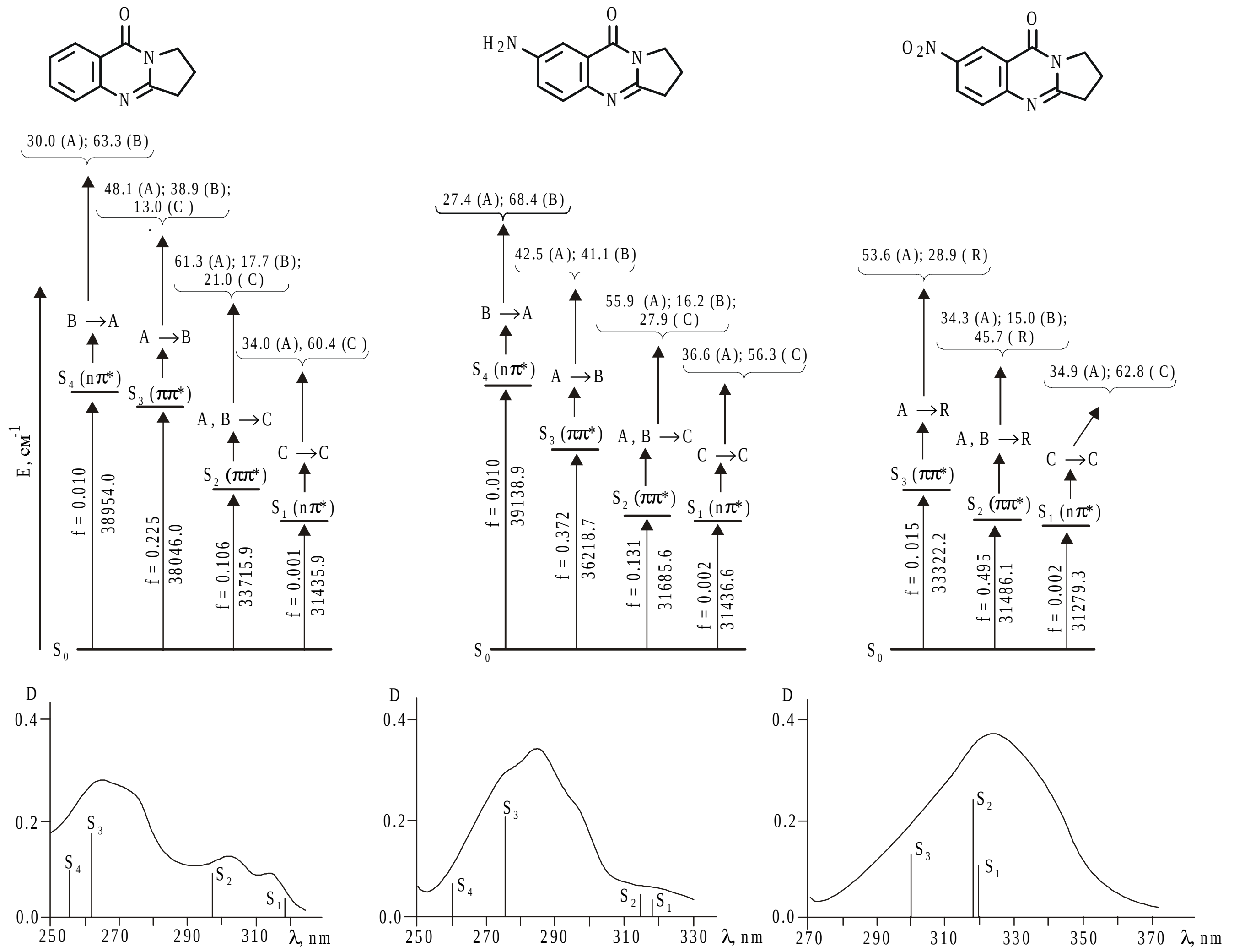
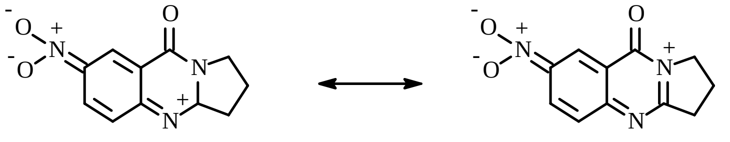


Fig. 1. Properties of electronic transitions and indices of electron-density distribution on atoms of fragments in the studied compounds for $S_0 \rightarrow S_k$ excitations.

The increase of total charge on the A and B fragments ($\Sigma\Delta q = -0.57\ e^-$) and rise in strength and lowering of the $S_0 \rightarrow S_2$ transition energy (Table 2 and Fig. 1, E = 31486.1 cm^{-1}, f = 0.495) on introducing the NO_2 group into **1** ($\Sigma\Delta q = -0.13\ e^-$, E = 33715.9, f = 0.303) leads to more effective charge transfer from the heterocyclic system onto the NO_2 group than onto the electron-accepting C=O of **1**. This causes a bathochromic shift in the spectrum of **3** and a strengthening of the band corresponding to the $S_0 \rightarrow S_2$ transition relative to that for **1** (Table 2 and Fig. 1).



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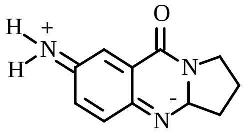

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Effective charge transfers between the A and B fragments in **2** and **3**, which to a first approximation do not affect the carbonyl, agree well with the structures of these compounds. In fact, the interaction of the carbonyl in **2** and **3** with the NH_2 and NO_2 groups in the *meta*-position of the benzene ring relative to them is minimal. However, their electronic effects are easily transmitted into fragment B, as can be seen in the limiting structures.

TABLE 3. Total Charge Changes of Molecular Fragments ($\Delta q_{\Phi p}$, e^-) and Their Contributions ($L\Phi_p$, %) to the Overall Molecular Electron-Density Distribution in $S_o \to S_k$ Excitations

$S_0 \to S_k$ transition	Configuration contributions	$\Delta q_{\Phi p}$, e^-				$L\Phi_p$, %				Assignment
		A	B	C	R	A	B	C	R	
Deoxyvasicinone (**1**)										
$S_0 \to S_1$	0.54 $\varphi_{3\to1'}$	0.28	0.04	-0.31	-	34.0	5.7	60.4	-	C→C
	0.20 $\varphi_{3\to4'}$	0.08	-	-0.1	-					
$S_0 \to S_2$	0.69 $\varphi_{1\to1'}$	-0.06	-0.07	0.13	-	61.3	17.7	21.0	-	A,B→C
$S_0 \to S_3$	0.67 $\varphi_{1\to2}$	-0.20	0.16	0.03	-	48.2	38.9	13.0	-	A→B
$S_0 \to S_4$	0.67 $\varphi_{5\to2''}$	0.12	-0.16	0.06	-	30.0	63.3	6.7	-	B→A
6-Aminodeoxyvasicinone (**2**)										
$S_0 \to S_1$	0.52 $\varphi_{4\to1'}$	0.26	-0.02	-0.22	-	36.6	7.0	56.3	-	C→C
$S_0 \to S_2$	0.77 $\varphi_{1\to1'}$	-0.5	-0.11	0.19	-	55.9	16.2	27.9	-	A,B→C
$S_0 \to S_3$	0.82 $\varphi_{1\to2'}$	-0.24	0.29	0.02	-0.07	42.5	41.1	6.8	9.6	A→B
$S_0 \to S_4$	0.74 $\varphi_{5\to2'}$	0.12	-0.14	0.04	-	27.4	68.4	4.2	-	B→A
6-Nitrodeoxyvasicinone (**3**)										
$S_0 \to S_1$	0.65 $\varphi_{3\to2'}$	0.36	-	-0.29	-					
	0.22 $\varphi_{3\to5'}$	0.09	0.01	-0.10	-	34.9	-	62.8	-	C→C
$S_0 \to S_2$	0.92 $\varphi_{1\to1'}$	-0.36	-0.21	-0.07	0.64	34.3	15.0	5.0	45.7	A,B→R
$S_0 \to S_3$	0.46 $\varphi_{1\to2'}$	-0.26	0.01	-0.02	0.27					
	0.37 $\varphi_{2\to1'}$	-	-0.06	0.07	-	53.6	7.2	10.3	28.9	A→R

TABLE 4. Population of pz-AO of Atoms in **1-3**

Compound	Atoms					
	C(2)	C(5)	C(7)	N(1)	N(3)	O
1	0.926	0.945	0.965	1.262	1.664	1.444
2	0.939	1.009	1.019	1.192	1.666	1.445
3	0.895	0.862	0.903	1.225	1.651	1.429

Thus, analysis of the electron-density distribution in the excited states elucidated the principal types of electronic transitions responsible for the absorption spectra of **1-3**.

EXPERIMENTAL

UV spectra were measured on a Perkin—Elmer Lambda-16 spectrometer in ethanol using 1-cm quartz cuvettes and solution concentrations $5\cdot10^{-5}$-$5\cdot10^{-4}$ M.

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