

NATURE OF π -ELECTRON TRANSITIONS IN THE SPECTRA OF 2,3-POLYMETHYLENE- 3,4-DIHYDRO-4-QUINAZOLONES AND THEIR ANALOGS

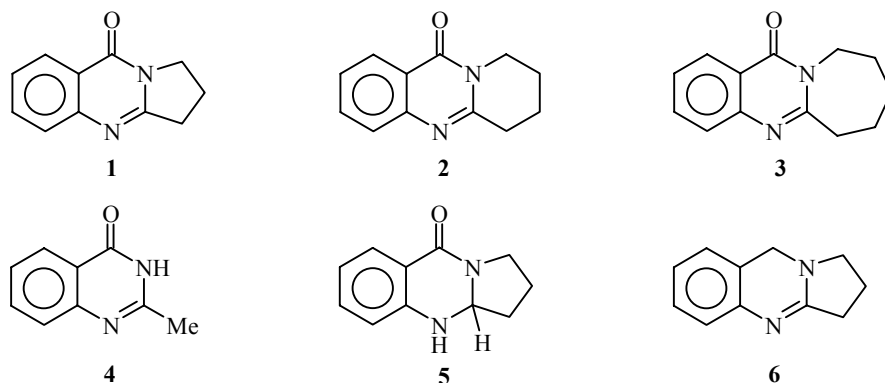
E. L. Kristallovich, A. G. Eshimbetov, and Kh. M. Shakhidoyatov

We have studied the nature of electronic transitions in the UV spectra of 2,3-polymethylene-3,4-dihydro-4-quinazolones and their analogs. The results of LCAO MO quantum chemical calculations in the ZINDO/S approximation, taking into account configuration interaction, correlate satisfactorily with the positions of the bands in the experimental spectra of the studied compounds.

Keywords: 4-quinazolones, quantum-chemical calculations, UV spectra.

Study of the characteristic features of electronic transitions in 2,3-poly(tri-, tetra-, penta)methylene-3,4-dihydro-4-quinazolones **1-3** is of considerable interest for prediction of spectral effects in synthetic drugs [1-5]. These compounds, differing in the size of one of the rings, differ considerably in reactivity with respect to reduction of the carbonyl group, the double bond N=C, and also in reactions of their α -methylene group with electrophilic reagents [6].

Continuing our systematic quantum chemical studies of quinazolone derivatives [7, 8], in this work we calculated the UV spectra of compounds **1-3**, their bicyclic analog 2-methyl-4-quinazolone (**4**), 1,2-dihydro-2,3-trimethylene-1,2,3,4-tetrahydro-4-quinazolone (**5**), and also the product of reduction of the CO group of compound **1**: 2,3-trimethylene-3,4-dihydroquinazoline (**6**). All these compounds are characterized by a common structural fragment N(1)=C(2)-N(3)-C(4).



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The calculations of the electronic spectra were performed by the ZINDO/S semi-empirical method [9, 10] for a molecular geometry that was fully optimized by the PM3 method [11], taking into account configuration interaction between the six occupied and unoccupied MO's (73 singly excited configurations). We used the Hyperchem 6.0 software packages (Hypercube, Inc.)

The two-center Coulomb integrals $\gamma_{\mu\nu}$ were calculated using the Mataga–Nishimoto formula [12]:

$$\gamma_{\mu\nu} = \frac{f_r}{a_{\mu\nu} + R_{\mu\nu}}, \quad a_{\mu\nu} = \frac{2f_r}{\gamma_{\mu\mu} + \gamma_{\nu\nu}} \quad (1)$$

where $R_{\mu\nu}$ is the bond length, f_r is a constant equal to 1.2. The one-center Coulomb integrals $\gamma_{\mu\mu}$ are usually taken to be equal to the differences between the ionization potential and the electron affinity of the atoms. In the ZINDO/S method, the resonance integral $\beta_{\mu\nu}$ is calculated using formula (2) with overlap integral ($S_{\mu\nu}$) decomposed into σ - and π -components:

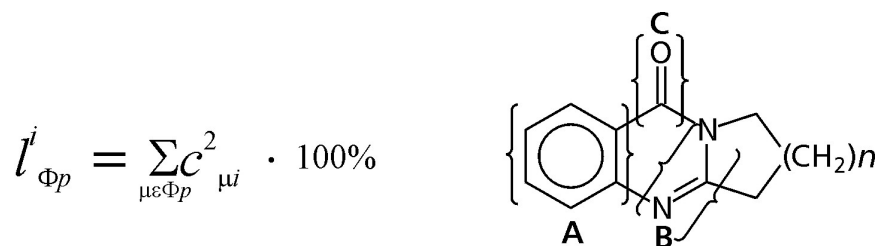
$$\beta_{\mu\nu} = 1/2(\beta_A^0 + \beta_B^0)(k_1 S_{\mu\nu}^\sigma + k_2 S_{\mu\nu}^\pi), \quad (2)$$

where β_A^0 and β_B^0 are empirical parameters characteristic for each atom, k_1 and k_2 are adjusted coefficients (weighting factors) equal to 1.267 and 0.585 respectively.

Within the framework of MO theory taking into account configuration interaction (CI), the shape of the wave functions for the ground state (φ_i) and the excited state (φ_j) reflects their structural features, and this fact was used to classify the electronic transitions (Tables 1 and 2). Each one-electron π -MO was represented by a set of symbols for the fragments of the molecule on which this MO was predominantly localized.

For a qualitative estimate of the localization of the electronic transitions in molecules **1-6**, we considered the individual fragments **A**, **B**, **C**, which make a substantial contribution to formation of one of the MO's.

The degree of localization on individual parts of the molecule is expressed by the sum of the squares of the coefficients for the basis AO's of the fragments [13-15].



The results of the quantum chemical calculations of the UV spectra for compounds **1-6** are shown in Tables 1 and 2 and in Figs. 1 and 2. Comparing the data in Fig. 1 and Table 2, we can trace the genetic relationship between the electronic transitions in the experimental and calculated absorption spectra for compounds **1-3** and their structural analog **4**.

Comparison of the data in Table 2 allows us to assign the absorption band in the 315±4 nm region to the $n \rightarrow \pi^*$ electronic transition of fragment **C** (318±5 nm), since single excited configurations ($\varphi_3 \rightarrow \varphi_j$) make a contribution to the considered transition $\psi_0 \rightarrow \psi_1$ specifically with participation of those orbitals (Table 1). The correctness of this assignment is supported by the similarity of the long-wavelength transition in the theoretical spectra of compounds **1-4** and the transition $\psi_0 \rightarrow \psi_1$ in the spectrum of compound **5** ($n \rightarrow \pi^*$), and also the change in the nature of this electronic transition ($\pi \rightarrow \pi^*$) and the absence of an absorption band in the

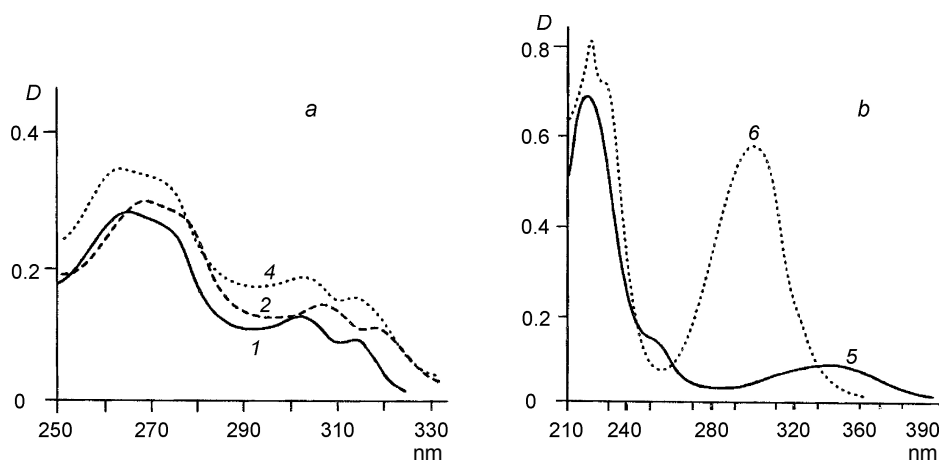


Fig. 1. UV spectra (in ethanol): *a*) compounds **1** (1), **2** (2), and **4** (4); *b*) compounds **5** (5) and **6** (6).

310-340 nm region in the spectrum of compound **6** (Table 2, Fig. 1*b*). The absorption band at a wavelength of 304 ± 2 nm (Fig. 1*a*, Table 2), belonging to the one-configuration transition $\psi_0 \rightarrow \psi_2$ (297 ± 2 nm), is due to charge transfer from fragments **A** and **B** to fragment **C**.

As follows from the data given in Table 2 and in Fig. 3, in the absorption spectra of compounds **1-4** we observe two transitions ($\psi_0 \rightarrow \psi_3$ and $\psi_0 \rightarrow \psi_4$ in the 260-290 nm region), localized on the fragments **A** ($\pi \rightarrow \pi^*$) and **B** ($n \rightarrow \pi^*$) respectively, where the band connected with excitation of fragment **B** ($n \rightarrow \pi^*$), due to low intensity, overlaps with the absorption band due to the $\pi \rightarrow \pi^*$ electronic transition in the benzene fragment, as is observed in the spectra of isoquinoline [10] and 2,3-trimethylene-3,4-dihydroquinazoline (**6**). This conclusion is supported by the complicated shape of the band in the 260-290 nm region, as the envelope of two individual absorption bands ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) in the experimental spectra of compounds **1-4**. The $\psi_0 \rightarrow \psi_4$ electronic transition (231 ± 1 nm) in the spectra of compounds **1-4** occurs upon local excitation of the benzene fragment.

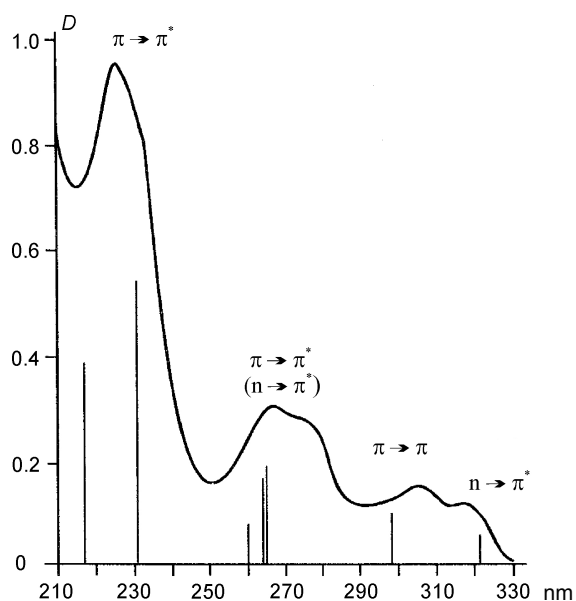


Fig. 2. UV spectra (in ethanol) of compound **3**: vertical lines = calculated transitions.

TABLE 1. Basic Characteristics of MO's and Contributions of Fragments to MO's of Compounds **1-6**

Com- pound	MO	Energy of MO, eV	Type of MO	Contributions of fragments to MO*, %		
				A	B	C
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	-8.25	π	66.6	25.2	6.7
	φ_2	-9.14	π	90.0	—	7.3
	φ_3	-9.99	n	6.4	8.0	77.3
	φ_4	-10.29	π	23.6	52.6	15.5
2	φ_4'	1.76	π^*	53.9	12.3	32.7
	φ_3'	1.25	π^*	66.1	23.1	10.2
	φ_2'	0.07	π^*	37.1	47.0	14.2
	φ_1'	-0.13	π^*	55.9	18.7	24.1
	φ_1	-8.22	π	65.6	26.2	6.8
	φ_2	-9.13	π	91.3	—	7.9
	φ_3	-9.99	n	7.9	7.1	80.8
	φ_4	-10.31	π	20.8	63.8	9.8
3	φ_4'	1.76	π^*	44.6	8.7	34.7
	φ_3'	1.26	π^*	49.3	23.3	10.6
	φ_2'	0.09	π^*	36.9	47.2	13.2
	φ_1'	-0.12	π^*	55.8	16.7	25.4
	φ_1	-8.22	π	65.5	24.1	6.6
	φ_2	-9.12	π	90.7	—	7.6
	φ_3	-9.94	n	6.8	5.2	84.0
	φ_4	-10.28	π	24.6	52.8	—
4	φ_4'	1.70	π^*	51.2	12.1	35.0
	φ_3'	1.17	π^*	64.2	24.4	9.3
	φ_2'	0.00	π^*	36.1	45.3	14.2
	φ_1'	-0.21	π^*	54.5	18.0	23.7
	φ_1	-8.32	π	67.2	24.6	4.7
	φ_2	-9.21	π	90.0	0.3	8.0
	φ_3	-10.06	n	5.2	7.4	82.1
	φ_4	-10.55	n	15.3	72.4	1.3
5	φ_2'	0.66	π^*	97.1	1.3	—
	φ_1'	-0.06	π^*	63.0	3.1	27.8
	φ_1	-8.52	π	74.4	18.5	2.0
	φ_2	-9.23	π	90.6	—	7.3
	φ_3	-9.64	n	2.8	43.2	41.8
	φ_4	-10.03	n	6.4	26.5	57.7
6	φ_4'	2.97	π^*	20.8	28.4	—
	φ_3'	1.73	π^*	49.1	35.4	—
	φ_2'	1.09	π^*	96.9	—	—
	φ_1'	0.45	π^*	40.3	55.2	—
	φ_1	-7.73	π	67.0	27.5	—
	φ_2	-8.58	π	93.5	1.4	—
	φ_3	-9.84	n	19.0	71.5	—
φ_4	-10.36	n	27.5	62.3	—	

* Fragment contributions less than 5% were neglected.

TABLE 2. Calculated and Experimental Characteristics of the UV Spectra of Compounds 1-6

Com- pound	Transition $\Psi_0 \rightarrow \Psi_k$	Configurational composition	Type of transition	$\lambda_{\text{max}}^{\text{calc}}$, nm	Experiment	
					λ_{max} , nm	log ϵ
1	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_1'$ (0.53)	$n \rightarrow \pi^*$	318.1	314.0	3.80
		$\varphi_3 \rightarrow \varphi_4'$ (0.32)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_1'$ (0.59)	$\pi \rightarrow \pi^*$	296.6	302.0	3.83
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_2'$ (0.58)	$\pi \rightarrow \pi^*$	262.8	265.0	4.04
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_5 \rightarrow \varphi_2'$ (0.58)	$n \rightarrow \pi^*$	256.7		
	$\Psi_0 \rightarrow \Psi_5$	$\varphi_1 \rightarrow \varphi_2'$ (-0.34)	$\pi \rightarrow \pi^*$	231.2	225.0	4.55
$\varphi_1 \rightarrow \varphi_3'$ (0.33)						
$\varphi_2 \rightarrow \varphi_1'$ (-0.41)						
$\Psi_0 \rightarrow \Psi_6$	$\varphi_2 \rightarrow \varphi_2'$ (-0.56)	$\pi \rightarrow \pi^*$	217.5			
2	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_1'$ (0.50)	$n \rightarrow \pi^*$	323.5	318.0	3.52
		$\varphi_3 \rightarrow \varphi_2'$ (0.32)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_1'$ (0.59)	$\pi \rightarrow \pi^*$	298.9	306.0	3.61
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_2'$ (0.58)	$\pi \rightarrow \pi^*$	266.4	268.0	3.91
		$\varphi_5 \rightarrow \varphi_2'$ (0.58)	$n \rightarrow \pi^*$			
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_1 \rightarrow \varphi_2'$ (0.35)	$\pi \rightarrow \pi^*$	265.6		
$\Psi_0 \rightarrow \Psi_5$	$\varphi_1 \rightarrow \varphi_2'$ (0.33)	$\pi \rightarrow \pi^*$	232.3	226.0	4.33	
	$\varphi_1 \rightarrow \varphi_3'$ (-0.34)					
	$\varphi_2 \rightarrow \varphi_1'$ (-0.42)					
$\Psi_0 \rightarrow \Psi_6$	$\varphi_2 \rightarrow \varphi_2'$ (-0.56)	$\pi \rightarrow \pi^*$	218.7			
3	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_2'$ (0.52)	$n \rightarrow \pi^*$	322.7	317.0	3.51
		$\varphi_3 \rightarrow \varphi_4'$ (0.32)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_1'$ (0.59)	$\pi \rightarrow \pi^*$	298.3	305.0	3.60
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_2'$ (0.58)	$\pi \rightarrow \pi^*$	265.2		
		$\varphi_5 \rightarrow \varphi_2'$ (0.58)	$n \rightarrow \pi^*$			
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_1 \rightarrow \varphi_2'$ (0.42)	$\pi \rightarrow \pi^*$	263.2	267.0	3.91
$\varphi_5 \rightarrow \varphi_2'$ (0.39)		$n \rightarrow \pi^*$				
$\Psi_0 \rightarrow \Psi_5$	$\varphi_5 \rightarrow \varphi_2'$ (-0.52)	$n \rightarrow \pi^*$	260.0	225.0	4.51	
	$\varphi_1 \rightarrow \varphi_2'$ (-0.34)					
	$\varphi_1 \rightarrow \varphi_3'$ (-0.33)					
$\Psi_0 \rightarrow \Psi_6$	$\varphi_2 \rightarrow \varphi_1'$ (0.41)	$\pi \rightarrow \pi^*$	230.9	225.0	4.51	
	$\varphi_2 \rightarrow \varphi_2'$ (-0.55)					
4	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_1'$ (0.50)	$n \rightarrow \pi^*$	318.1	315.0	3.44
		$\varphi_3 \rightarrow \varphi_2'$ (-0.33)				
		$\varphi_3 \rightarrow \varphi_4'$ (-0.32)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_1'$ (0.58)	$\pi \rightarrow \pi^*$	296.6	304.0	3.52
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_2'$ (0.55)	$\pi \rightarrow \pi^*$	262.8	263.0	3.77
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_4 \rightarrow \varphi_2'$ (0.56)	$n \rightarrow \pi^*$	256.7	224.0	4.31
$\varphi_1 \rightarrow \varphi_2'$ (-0.34)						
$\Psi_0 \rightarrow \Psi_5$	$\varphi_1 \rightarrow \varphi_3'$ (0.33)	$\pi \rightarrow \pi^*$	231.2	224.0	4.31	
	$\varphi_2 \rightarrow \varphi_1'$ (-0.43)					
	$\varphi_2 \rightarrow \varphi_2'$ (0.59)					
$\Psi_0 \rightarrow \Psi_6$	$\varphi_2 \rightarrow \varphi_2'$ (0.59)	$\pi \rightarrow \pi^*$	217.4			
5	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_1'$ (0.38)	$n \rightarrow \pi^*$	334.9	335.0	3.52
		$\varphi_4 \rightarrow \varphi_1'$ (-0.38)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_1'$ (0.56)	$\pi \rightarrow \pi^*$	288.2		
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_1'$ (0.33)	$\pi \rightarrow \pi^*$	241.5	257.0 _{sh}	3.72
		$\varphi_1 \rightarrow \varphi_2'$ (-0.41)				
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_2 \rightarrow \varphi_1'$ (-0.38)	$\pi \rightarrow \pi^*$	212.9	222.0	4.58
$\varphi_2 \rightarrow \varphi_1'$ (0.37)						
6	$\Psi_0 \rightarrow \Psi_1$	$\varphi_3 \rightarrow \varphi_1'$ (0.53)	$n \rightarrow \pi^*$	264.0	220.0	3.93
		$\varphi_4 \rightarrow \varphi_1'$ (0.34)				
	$\Psi_0 \rightarrow \Psi_2$	$\varphi_1 \rightarrow \varphi_2'$ (0.49)	$\pi \rightarrow \pi^*$	286.8	299.0	3.71
		$\varphi_2 \rightarrow \varphi_1'$ (0.37)				
	$\Psi_0 \rightarrow \Psi_3$	$\varphi_1 \rightarrow \varphi_1'$ (0.65)	$\pi \rightarrow \pi^*$	276.5		
	$\Psi_0 \rightarrow \Psi_4$	$\varphi_1 \rightarrow \varphi_3'$ (-0.57)	$\pi \rightarrow \pi^*$	214.2	220.0	3.93
$\varphi_2 \rightarrow \varphi_2'$ (-0.32)						
$\Psi_0 \rightarrow \Psi_5$	$\varphi_1 \rightarrow \varphi_2'$ (0.37)	$\pi \rightarrow \pi^*$	208.8			
	$\varphi_2 \rightarrow \varphi_1'$ (0.52)					

We should note that evidence for the validity of the study comes from the fact that the quantum-chemical calculations reflect the experimentally observed way that the bands shift in the 260-270 nm and 290-320 nm regions as the ring sizes change.

Thus, using quantum-chemical calculations in the ZINDO/S approximation taking into account CI, we have established the nature of the electronic transitions in the UV spectra of 2,3-polymethylene-3,4-dihydro-4-quinazolones and their analogs. We obtained a satisfactory correlation between the positions of the bands in the experimental and theoretical spectra of the studied compounds.

EXPERIMENTAL

The UV spectra were measured on a Perkin-Elmer Lambda-16 spectrometer in ethanol solution in a quartz cuvet 1 cm thick, for a concentration of the solutions equal to $5 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ M.

The synthesis and physicochemical characteristics of the studied compounds are described in [16, 17].

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