Electron affinity and ultraviolet absorption spectra of (*E*)-β-nitrostyrenes

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The UV-VIS spectra of (*E*)-β-nitrostyrenes were measured. It was stated, by means of CNDO/S calculations, that a long-wavelength band corresponds to the electron transfer from the HOMO to LUMO level, while the short-wavelength one originates from the transitions $\psi_{HOMO-2} \rightarrow \psi_{LUMO}$ and $\psi_{HOMO-1} \rightarrow \psi_{LUMO+1}$. On the basis of the energy of the former band the electron affinity of these compounds was approximated.

Prediction of the regioselectivity of chemical reactions on the basis of Salem—Klopman's equation [1] demands the knowledge of the electron affinity (A) of substrates. The precise A values are provided by magnetotronic measurements [2, 3] and by mass spectrometry of negative ions [4, 5]. Both these techniques are, however, expensive and they require use of highly specialized equipment. In the case of homogeneous series of compounds satisfactory A values can be obtained on the basis of the orbital theory of electron excitations [6], by utilizing easily available electronic spectra. In view of this theory the electronic transition from the ground to excited singlet state corresponds to the electron transfer from an occupied orbital ψ_i to an unoccupied virtual orbital ψ_j. The energy of such a transition is expressed by the equation

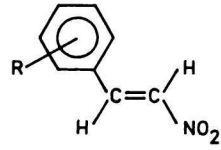
$$\Delta E_{ij} = \varepsilon_j - \varepsilon_i + (2K_{ij} - J_{ij}) \qquad (1)$$

where ε_i, ε_j stand for energies of the orbitals ψ_i and ψ_j, while K_{ij} and J_{ij} stand for coulombic and resonance integrals, respectively. The term $(2K_{ij} - J_{ij})$ for homogeneous series remains relatively constant [6, 7]. Therefore taking into account Koopman's theorem [8] it can be concluded that the electron affinity of the compound can be approximated by the equation

$$A = I - \Delta E' - \Delta \qquad (2)$$

in which I is the first ionization potential, $\Delta E'$ is the energy of the electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and Δ represents a constant characteristic for the series.

In this contribution eqn (*2*) was used for calculation of the electron affinity of *meta*- and *para*-substituted *E*-β-nitrostyrenes *I*—*X*. We test these compounds as dipolarophiles in cycloaddition reactions with *N*-oxides of nitriles.



	I	*II*	*III*	*IV*	*V*
R:	*p*-OCH_3	*p*-CH_3	*m*-CH_3	H	*p*-F
	VI	*VII*	*VIII*	*IX*	*X*
R:	*p*-Cl	*m*-Cl	*p*-Br	*p*-C≡N	*p*-NO_2

In order to specify the energy of the electron transfer from the HOMO to the LUMO UV—VIS spectra of the compounds studied were measured in n-hexane and identification of the absorption bands was done. It was found that in the near ultraviolet range the spectra of *I*—*X* comprise two characteristic bands. The first, less intensive band, occurs in the range of $\lambda = 220$—240 nm, while the second one is placed in the region of 280—330 nm (Table 1). In many aspects these spectra are similar to the spectra of the corresponding derivatives of nitrobenzene and *p*-substituted styrenes. On this ground *Skulski* and *Urbański*

Table 1

Positions of the UV—VIS spectra maximums, ionization potentials and electron affinity of (*E*)-β-nitrostyrenes

Compound	Band ^1B		Band ^1L_a			$\frac{I}{eV}$	$\frac{A}{eV}$
	$\frac{\lambda_{max}}{nm}$	$\frac{\log \varepsilon}{m^2 mol^{-1}}$	$\frac{\lambda_{max}}{nm}$	$\frac{\log \varepsilon}{m^2 mol^{-1}}$	$\frac{\Delta E'}{eV}$		
I	238	5.02	330	5.29	3.76	8.50	1.14
II	230	5.00	310	5.27	4.00	8.79	1.19
III	228	5.01	304	5.21	4.08	8.93	1.25
IV	225	5.02	297	5.22	4.18	9.12	1.35
V	227	4.98	301	5.18	4.12	9.25	1.33
VI	228	5.04	305	5.25	4.07	9.04	1.37
VII	229	5.06	308	5.31	4.03	8.96	1.34
VIII	230	5.06	294	5.20	4.22	9.22	1.40
IX	<220	—	291	5.21	4.26	9.56	1.70
X	<220	—	289	5.23	4.29	9.83	1.94

[9] put forward the hypothesis that the long-wavelength band in β-nitrostyrenes comes from the ^1L_a band of benzene, while the short-wavelength band comes from the band ^1B.

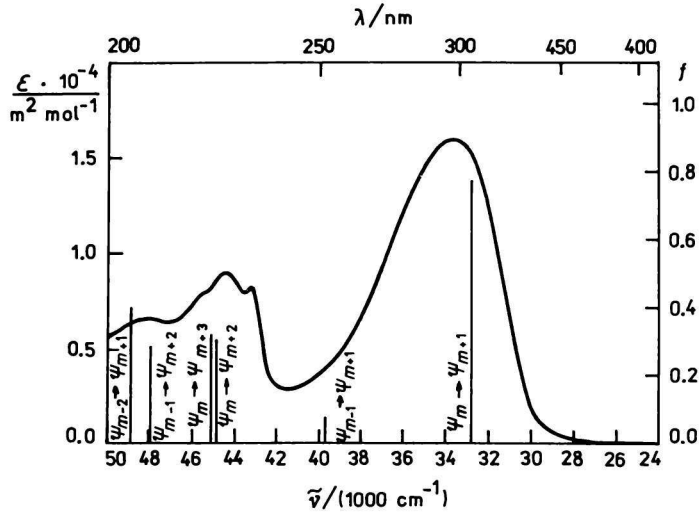


Fig. 1. UV—VIS spectrum of (*E*)-β-nitrostyrene and its theoretical interpretation according to CNDO/S method

In order to confirm this suggestion we calculated the electron-transition energy and the corresponding oscillator strength for the compounds *I*—*V* and *IX* by the CNDO/S method. As it appears from Fig. 1 and from the data in Tables 1 and 2 the agreement between the calculation and the experimental results is satisfactory, although, in the calculation the configuration interactions (C1) were disregarded. It is evident from the calculations that the band ^1L_a in β-nitrostyrenes corresponds to the electron transfer from the highest occupied level ψ_m to the adjacent higher level ψ_{m+1}. On the other hand, the band interpreted as ^1B is the superposition of the two bands, which originate from the transitions $\psi_m \rightarrow \psi_{m+3}$ and $\psi_m \rightarrow \psi_{m+2}$. Moreover, the calculations suggest the presence of the weak band in the region of $\lambda = 245$—270 nm as well as the superposition of two bands in the region of $\lambda = 200$—220 nm. The former corresponds to the electron transfer from the level ψ_{m-1} to the level ψ_{m+1}, the latter comes from the transition from ψ_{m-2} to ψ_{m+1} and from ψ_{m-1} to ψ_{m+2}. They have, however, the minor influence on the shape of the band ^1L_a, which has been confirmed by calculations of the ^1L_a band contour by the moment method [10]. This is why in the calculation of the transition energy $\Delta E'$ (Table 2) the frequency corresponding to the maximum of the band ^1L_a was used. The

Table 2

Interpretation of the electron transitions in (*E*)-β-nitrostyrenes (CNDO/S computation data)

Compound	Transition orbitals[a]	Singlet states			Triplet states	
		$\Delta E'$ / eV	λ / nm	Oscillator strength	$\Delta E'$ / eV	λ / nm
I	$\psi_m \rightarrow \psi_{m+1}$	3.930	315.5	0.408	3.134	395.7
	$\psi_{m-6} \rightarrow \psi_{m+1}$	4.032	307.5	0.000	4.032	307.5
	$\psi_{m-5} \rightarrow \psi_{m+1}$	4.678	265.1	0.000	4.678	265.1
	$\psi_{m-1} \rightarrow \psi_{m+1}$	5.034	246.3	0.034	4.713	263.1
	$\psi_m \rightarrow \psi_{m+3}$	5.341	232.4	0.168	4.265	290.7
	$\psi_m \rightarrow \psi_{m+2}$	5.379	230.5	0.166	3.760	320.7
	$\psi_{m-1} \rightarrow \psi_{m+2}$	5.968	207.8	0.138	5.126	241.9
	$\psi_{m-2} \rightarrow \psi_{m+1}$	6.031	205.6	0.202	2.545	487.2
II	$\psi_m \rightarrow \psi_{m+1}$	3.941	314.6	0.395	3.167	391.5
	$\psi_{m-6} \rightarrow \psi_{m+1}$	4.491	276.1	0.000	4.491	276.1
	$\psi_{m-7} \rightarrow \psi_{m+1}$	4.713	263.1	0.000	4.713	263.1
	$\psi_{m-1} \rightarrow \psi_{m+1}$	5.000	247.9	0.034	4.696	264.0
	$\psi_m \rightarrow \psi_{m+3}$	5.392	229.9	0.171	4.305	288.0
	$\psi_m \rightarrow \psi_{m+2}$	5.418	228.8	0.170	3.799	326.3
	$\psi_{m-1} \rightarrow \psi_{m+2}$	5.950	208.4	0.139	5.110	242.6
	$\psi_{m-2} \rightarrow \psi_{m+1}$	6.039	205.3	0.204	2.493	497.3
III	$\psi_m \rightarrow \psi_{m+1}$	4.072	304.5	0.719	3.309	374.7
	$\psi_{m-6} \rightarrow \psi_{m+1}$	4.434	279.6	0.000	4.434	279.7
	$\psi_{m-7} \rightarrow \psi_{m+1}$	4.528	273.8	0.000	4.528	274.0
	$\psi_{m-1} \rightarrow \psi_{m+1}$	4.642	267.1	0.122	4.244	292.2
	$\psi_m \rightarrow \psi_{m+2}$	5.513	224.9	0.343	3.941	314.6
	$\psi_m \rightarrow \psi_{m+3}$	5.591	221.7	0.399	4.336	286.0
	$\psi_{m-1} \rightarrow \psi_{m+2}$	5.701	217.5	0.229	4.745	261.3
	$\psi_{m-2} \rightarrow \psi_{m+1}$	6.029	205.6	0.406	2.473	501.4
IV	$\psi_m \rightarrow \psi_{m+1}$	4.041	306.8	0.781	3.186	389.2
	$\psi_{m-6} \rightarrow \psi_{m+1}$	4.271	290.3	0.000	4.271	290.3
	$\psi_{m-1} \rightarrow \psi_{m+1}$	4.955	250.2	0.073	4.628	267.9
	$\psi_{m-7} \rightarrow \psi_{m+1}$	5.267	235.4	0.000	5.267	235.4
	$\psi_m \rightarrow \psi_{m+2}$	5.555	223.2	0.300	3.892	318.6
	$\psi_m \rightarrow \psi_{m+3}$	5.608	221.1	0.330	4.577	270.9
	$\psi_{m-4} \rightarrow \psi_{m+1}$	5.750	215.6	0.000	5.750	215.6
	$\psi_{m-1} \rightarrow \psi_{m+2}$	5.932	209.0	0.288	5.059	245.1
	$\psi_{m-2} \rightarrow \psi_{m+1}$	6.026	205.8	0.399	2.488	498.2

Table 2 (Continued)

Compound	Transition orbitals[a]	Singlet states			Triplet states	
		$\Delta E'$ / eV	λ / nm	Oscillator strength	$\Delta E'$ / eV	λ / nm
V	$\psi_m \rightarrow \psi_{m+1}$	4.008	309.3	0.408	3.160	392.3
	$\psi_{m-6} \rightarrow \psi_{m+1}$	4.697	304.7	0.000	4.070	304.7
	$\psi_{m-5} \rightarrow \psi_{m+1}$	4.883	253.9	0.000	4.883	253.9
	$\psi_{m-1} \rightarrow \psi_{m+1}$	5.088	243.7	0.040	4.748	261.1
	$\psi_m \rightarrow \psi_{m+3}$	5.396	229.8	0.165	4.338	285.8
	$\psi_m \rightarrow \psi_{m+2}$	5.439	228.0	0.152	3.799	326.4
	$\psi_{m-1} \rightarrow \psi_{m+2}$	5.983	207.2	0.147	5.124	242.0
	$\psi_{m-2} \rightarrow \psi_{m+1}$	6.252	205.8	0.196	2.582	480.2
IX	$\psi_m \rightarrow \psi_{m+1}$	4.392	282.3	0.570	3.179	390.0
	$\psi_{m-2} \rightarrow \psi_{m+1}$	4.613	268.8	0.000	4.613	268.8
	$\psi_{m-2} \rightarrow \psi_{m+3}$	4.825	257.0	0.000	4.825	257.0
	$\psi_{m-1} \rightarrow \psi_{m+1}$	4.943	250.8	0.095	4.081	303.1
	$\psi_m \rightarrow \psi_{m+2}$	5.587	221.9	0.074	4.756	260.7
	$\psi_m \rightarrow \psi_{m+3}$	5.681	218.3	0.173	4.527	273.9
	$\psi_{m-6} \rightarrow \psi_{m+1}$	5.736	216.2	0.000	5.736	216.2
	$\psi_{m-7} \rightarrow \psi_{m+1}$	5.934	208.9	0.000	5.934	208.9

a) ψ_m = HOMO; ψ_{m+1} = LUMO.

described types of the electron transitions are schematically shown on the example of β-nitrostyrene molecule (Fig. 2).

Apart from the singlet transitions in the near ultraviolet region, presence of the weak bands resulting from forbidden triplet transitions (oscillator strength $f = 0$) is also possible.

The ionization potentials applied in the calculation of electron affinity of the compounds *I*—*X* come from our earlier works [11, 12], in which they were measured by photoelectron spectroscopy (Table 1). In the meanwhile, we assumed the value of the constant $\Delta = 3.6$ as the typical value for styrene and its derivatives [13].

The electron affinity values of *I*—*X* approximated from eqn (*2*) are collected in Table 1. Attempts to estimate the regioselectivity of the [2 + 3] cycloaddition of nitrostyrenes *I*—*V* with benzonitrile *N*-oxide on the basis of the obtained *A* values revealed good agreement of the calculations with the experimental results. Detailed results will be published soon [14].

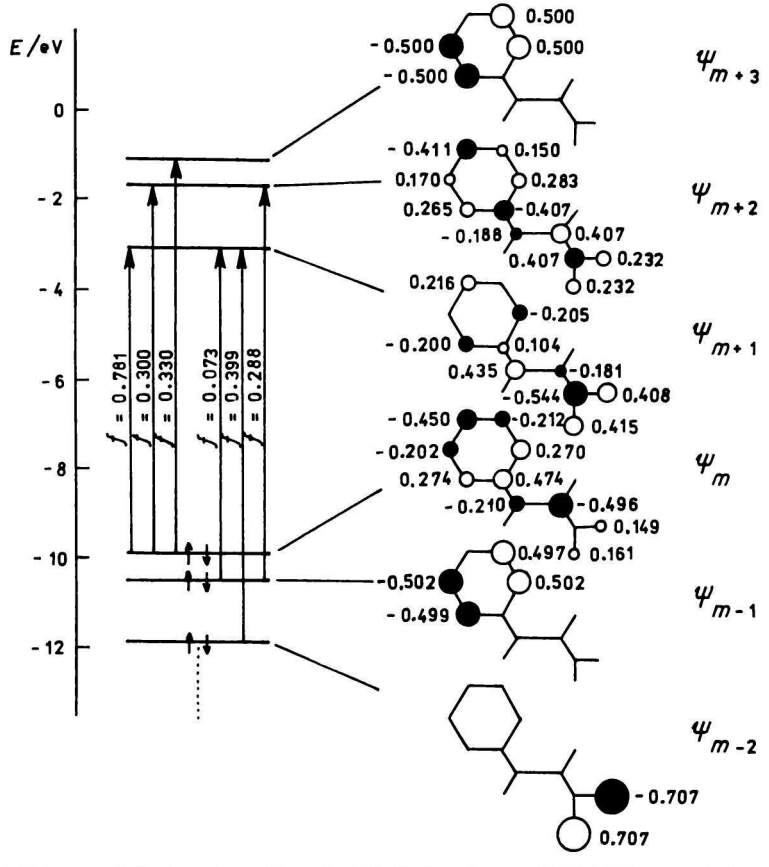


Fig. 2. Scheme of electron transitions in (*E*)-β-nitrostyrene (CNDO/S computation data).

Experimental

β-Nitrostyrenes *I*—*X* were synthesized from corresponding aromatic aldehydes and nitromethane according to the literature methods [15—17]. The ultraviolet absorption spectra were recorded in n-hexane on UV—VIS Specord instrument. Measurements were done three times for each compound and data given in Table 1 are the averages. Quantum-chemical calculations of the electron spectra were carried out by the CNDO/S program [18] in the Regional Computational Centre CYFRONET in Cracow, using CYBER-72 computer. Program performs orbital calculations for molecules in close-shell electronic configurations using parameters given by *Del Bene* and *Jaffe* [6, 19]. The two-centre two-electron repulsion integrals γ were evaluated by the Mataga approximation [6, 18]. The x, y, z coordinates of atoms were obtained by optimization of the structures of studied compounds with MNDO method [20].

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