UV SPECTRA OF N-VINYLPYRROLES

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The effect of the structure and the medium on the position and intensity of the absorption bands in the UV spectra that attest to the presence of a single conjugation system in N-vinylpyrroles is thoroughly analyzed. The tendency for a reduction in the intensity of the conjugation (disruption of the coplanarity) is appreciable as branching of the alkyl group in the 2 position increases. A pronounced interaction of the benzene and ethylene fragments through the pyrrole ring is observed.

Together with the discovery of the reaction between ketoximes and acetylene [1-3], which proceeds smoothly to give variously substituted N-vinylpyrroles, there have also appeared the possibility and necessity of a systematic investigation of their electronic structures as convenient models for a study of the interaction and transmission of the mutual effect of two unsaturated systems separated by a heteroatom.

The UV spectra of 2- and 3-alkyl-substituted N-vinylpyrroles (I-VIII) and annelated representatives of the IX-XI series consist of two bands at 200-206 and 247-254 nm (Table 2, Fig. 1). The introduction of phenyl substituents in the 2 and 3 positions of the pyrrole ring (XII-XIV) leads to the appearance in the spectra of a number of new high-intensity bands and to a pronounced hyperchromic effect in the region of the short-wave maximum (Fig. 2).

It is known [4, 5] that alkyl-substituted pyrroles have a single absorption maximum at 208-218 nm with an extinction of 2000-8000. It was assigned to a π-π^* transition from the results of quantum-mechanical calculations [6, 7]. One may note a tendency for a bathochromic shift and an increase in the intensity of this band as the number and donor strengths of the alkyl substituents increase [4, 5]. The introduction in the 2 position of the pyrrole ring of acceptor substituents that are capable of conjugation is accompanied by a hyperchromic effect and a pronounced bathochromic shift in the region of the normal pyrrole band [4, 5]. Almost nothing is known regarding the effect of unsaturated substituents attached to the nitrogen atom on the UV spectra of pyrroles. There are data [5] that N-acetylpyrrole absorbs at 239 nm (ε 10,800).

Thus, by comparing these data with the results obtained (Table 2 and Figs. 1 and 2), one may conclude that N-vinyl substitution in pyrrole gives an additional band at 247-254 nm and a certain hypsochromic shift of the usual maximum (8-12 nm). These changes are explainable by splitting of the electron levels and development of new π-π^* transitions, including those with reduced energy as a result of interaction of the higher orbitals of the two π systems. The hypsochromic shift in the region of the first maximum does not contradict this interpretation, inasmuch as more highly energetic π-π^* transitions also should arise with splitting of the interacting levels.

A comparison of the λ and ε values of alkyl-substituted (I-VIII) and annelated (IX-XI) N-vinylpyrroles shows that the influence of R and R' is a composite of their inductive and steric effects. The intensity of the band at ~200 nm increases systematically (up to 60%) as the total donor strength of R and R' increases

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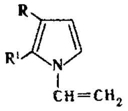
TABLE 1. Physicochemical Constants of N-Vinylpyrroles*



Compound	R	R′	bp, °C (mm)	d_4^{20}	n_D^{20}
I	H	CH_3	39—40 (10)	0,9308	1,5230
II	H	n-C_4H_9	74—75 (5)	0,9108	1,5150
III	H	tert-C_4H_9	73—74 (10)	0,9066	1,5130
IV	H	tert-C_4H_9	62—63 (10)	0,9275	1,5130
V	H	C_6H_{13}	112—113 (10)	0,8914	1,5040
VI	CH_3	CH_3	70—71 (20)	0,9297	1,5270
VII	CH_3	C_2H_5	59—60 (6)	0,9112	1,5185
VIII	n-C_3H_7	n-C_4H_9	86—87 (2)	0,8925	1,5025
IX	$(CH_2)_4$		91—92 (4)	1,0010	1,5560
X†	$CH(CH_3)(CH_2)_3$		68—69 (2)	0,9801	1,5465
XI	$(CH_2)_5$		73—74 (1)	0,9937	1,5560
XII	CH_3	C_6H_5	110 (1,5)	1,0509	1,5960
XIII	C_6H_5	C_6H_5	mp 125°	—	—

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*The purity of the compounds was higher than 98% according to the results of gas–liquid chromatography. All of the preparations were also characterized by NMR (^{1}H and ^{13}C) and IR spectroscopy, as well as by elementary analysis.

†Methyl group in the 7 position of the tetrahydroindole framework.

TABLE 2. UV Spectra* of N-Vinylpyrroles and 1-Ethyl-2-phenyl-3-methylpyrrole XIV

Compound	Cyclohexane		Ethanol	
	λ, nm	$\varepsilon \cdot 10^{-3}$	λ, nm	$\varepsilon \cdot 10^{-3}$
I	202	10,07	—	—
	248	12,86		
II	202	11,98	200	12,14
	252	13,13	250	12,29
III	201	11,81	201	10,92
	250	12,95	249	11,47
IV	202	12,20	—	—
	247	9,95		
V	205	12,78	—	—
	252	14,13		
VI	202	11,98	200	12,14
	251	13,36	249	13,37
VII	202	12,35	202	10,63
	254	12,63	254	9,79
VIII	201	12,30	200	12,41
	254	12,20	252	12,25
IX	203	12,24	202	11,19
	254	12,98	251	11,82
X	204	15,74	202	14,88
	254	15,20	252	13,74
XI	206	15,18	—	—
	251	10,65		
XII	200	20,06	200	19,07
	254	12,52	254	12,78
	270	13,55	268	13,14
XIII	202	32,55		
	223	21,97	—	—
	295	36,85		
	308	34,11		
XIV	203	16,15		
	218	10,28	—	—
	283	9,40		

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*Obtained with a Pye-Unicam SP-8000 spectrophotometer from solutions of 0,4-0,6 g of the substances per liter.

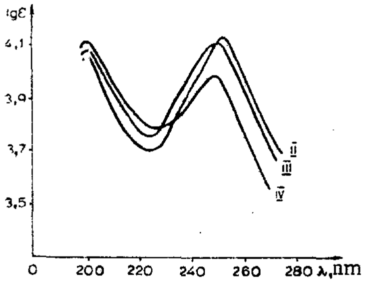

Fig. 1

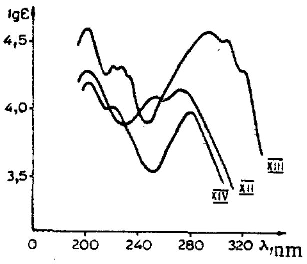

Fig. 2

Fig. 1. UV absorption spectra of alkyl-substituted N-vinylpyrroles (in cyclohexane).

Fig. 2. UV absorption spectra of 1-vinyl-2-phenyl-3-methylpyrrole (XII), 1-vinyl-2,3-diphenylpyrrole (XIII), and 1-ethyl-2-phenyl-3-methylpyrrole (XIV) (in cyclohexane).

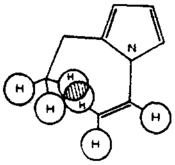

Fig. 3

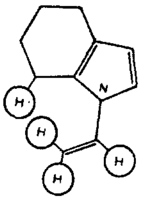

Fig. 4

Fig. 3. Steric hindrance to coplanarity in 1-vinyl-2-tert-butyl-pyrrole IV.

Fig. 4. Absence of steric hindrance to coplanarity in 1-vinyl-4,5,6,7-tetrahydroindole (IX).

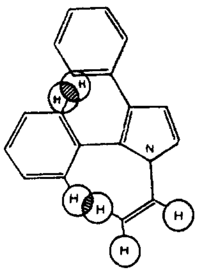

Fig. 5. Steric hindrance to coplanarity in 1-vinyl-2,3-diphenylpyrrole.

(with respect to the Taft σ^* scale). The long-wave band is more sensitive to the steric effect of the group in the 2 position; ε decreases (up to 30%) as the group in the 2 position becomes branched, during which there is a simultaneous blue shift of the maximum (compare II, III, and IV). The projection diagram (Fig. 3) for 1-vinyl-2-tert-butyl-3-methylpyrrole (IV) confirms that at least one of the planar conformations of this compound is actually sterically hindered.* In this case the steric effect is satisfactorily interpreted as inhibition of conjugation between the pyrrole ring and the vinyl group due to distortion of the coplanarity of the system. One observes intensification of the signs of conjugation (an increase in the ε value of the band at ~250 nm) when, through annelation, the carbon chain of the substituent in the 2 position is rigidly fixed on the same side as the N-vinyl grouping, as in 1-vinyl-4,5,6,7-tetrahydroindole (IX) (Fig. 4). The retention of a high ε value (15, 700) of the band at 254 nm in the spectrum of 1-vinyl-7-methyl-4,5,6,7-tetrahydroindole (X) makes it possible to assume that the cyclohexane fragment of this compound is at an angle with respect to the C_4-C_7 axis and the methyl group deviates appreciably from the plane of the conjugated system. Annelation with the seven-membered saturated ring (XI) apparently leads to angular strain in the pyrrole fragment and weakens the conjugation somewhat (the certain hypsochromic shift of the band at 251 nm with a simultaneous decrease in its intensity).

The spectra of phenyl-substituted N-vinylpyrroles (XII,XIII) indicate the development of a single system of conjugation including the benzene and pyrrole rings and the double bond. The spectrum of 1-vinyl-2-phenyl-3-methylpyrrole (XII) contains two maxima at 254 and 270 nm in the region of the "benzene" band (Fig. 2). Their intensities (12, 500 and 13,600, respectively) attest to the appearance of a new allowed trans-

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*An interaction radius of 0.6 Å [4, 8] was used in the construction of the diagram for the hydrogen atom. If one proceeds from the basis of the van-der-Waals radius (1.1 Å), the second planar conformation also proves to be sterically hindered.

ition, i.e., to additional interaction of the π orbitals. A second phenyl ring in the 3 position (XIII) sharply deepens the conjugation, as expressed in the strong bathochromic shifts of the long-wave bands (30-40 nm), the almost threefold increase in their intensities (34, 100-36, 900), and the appearance of a long-wave band at 321 nm (ε 20, 400). At the same time, the ε value of the band at ~200 nm, which corresponds to higher-energy transitions, is made up approximately additively from the molar extinction coefficients of the N-vinylpyrrole and benzene rings. Consequently, the conjugation affects mainly the high-lying electron levels. One must also bear in mind that the 1-vinyl-2,3-diphenylpyrrole molecule (XIII) cannot be coplanar (Fig. 5), and, consequently, in this case there is only partial overlapping of the π orbitals. The existence of conjugation between the vinyl group and the benzene ring, transmitted through the pyrrole ring, also follows unambiguously from a comparison of the UV spectra of 1-vinyl-2-phenyl-3-methylpyrrole (XII) and the corresponding ethyl derivative (XIV). Replacement of the vinyl group attached to the nitrogen atom by an ethyl group leads to radical changes inthe spectrum (Fig. 2): A strong hypsochromic shift of one of the long-wave bands (36 nm) is observed, while the other undergoes an appreciable bathochromic shift (13 nm), during which the oscillator forces fall sharply for both groups of transitions (Table 2). It is interesting that in this case the "pyrrole" band (~200 nm) reacts extremely weakly to the changes in the structure of the molecule.

The solvent effect observed on passing from cyclohexane to ethanol (Table 2) can be interpreted as additional evidence in favor of conjugation between the pyrrole ring and the vinyl group. Ethanol, by forming a hydrogen bond with the π system of pyrrole, somewhat reduces the ability of the nitrogen atom to participate in conjugation. This is expressed in the weak (1-3 nm) hypsochromic shifts, which are accompanied, as a rule, by an appreciable hypochromic effect (~10%); this is rather unusual for π-π^* bands, which most often undergo bathochromic shifts in more polar solvents.

LITERATURE CITED

1. B. A. Trofimov, A. S. Atavin, G. A. Kalabin, A. I. Mikhaleva, and E. G. Chebotareva, Zh. Organ. Khim., 9, 2205 (1973).
2. B. A. Trofimov, S. E. Korostova, and L. N. Balabanova, Khim. Geterotsikl. Soedin. (1975, in press).
3. B. A. Trofimov, G. A. Kalabin, A. S. Atavin, A. I. Mikhaleva, and E. G. Chebotareva, Khim. Geterotsikl. Soedin., 360 (1975).
4. G. F. Bol'shakov, V. S. Vatago, and F. B. Agrest, Ultraviolet Spectra of Heteroorganic Compounds [in Russian], Khimiya, Leningrad (1969), p. 22.
5. A. Stern and K. Timmons, Electronic Absorption Spectroscopy in Organic Chemistry [Russian translation], Mir, Moscow (1974), p. 195.
6. N. Solony and F. W. Birss, Canad. J. Chem., 43, 1569 (1965).
7. L. I. Lagut-skaya, Teor. i Éksperim. Khim., 9, 159 (1973).
8. E. A. Braude and F. Sondheimer, J. Chem. Soc., 3754 (1954).