INTRAMOLECULAR INTERACTIONS IN VINYLOXYQUINOLINES

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UDC 547.831.7:543.422.6:541.67

The UV spectra of 2-, 3-, 4-, 6-, and 8-vinyloxyquinolines were obtained, and their structures were subjected to quantum-chemical calculation within the Pariser—Parr—Pople (PPP) π-electron approximation in order to ascertain the effect of the vinyloxy group on the nature of their electron transitions and on their electronic structures. A linear relationship between the difference in the π charges on the carbon atoms of the vinyl group and its integral intensity in the IR spectra was established. As a result it was concluded that there is an analogy between the orienting effect of the substituents in benzenes and the interaction of the vinyloxy group with the nitrogen atom in vinyloxyquinolines. The polarity of the vinyl group in vinyloxyquinoline hydrochlorides was estimated on the basis of the established dependence.

The presence of substituents in various positions of the ring of heterocyclic molecules has a substantial effect on their reactivities. Many reactions of vinyloxyquinolines (VOQ) proceed with the participation of the vinyl group [1]. In this connection, we studied the interaction of the quinoline ring and the $CH_2{=}CH{-}O$ group as a function of its position relative to the nitrogen atom.

In the present research we analyzed the UV absorption spectra and calculated the structure of 2-, 3-, 4-, 6-, and 8-VOQ within the π-electron approximation. The geometry of the compounds and the numbering of the atoms are given in Fig. 1. The features of the computational scheme of the Pariser—Parr—Pople (PPP) method are described in [2]. The variable semiempirical parameters have the following values:

TABLE 1. Calculated and Experimentally Determined Energies of the Electron Transitions (in electron volts)

Quinoline (I)				2-Vinyloxyquinoline (II)				3-Vinyloxyquinoline (III)			
calc.		exptl.		calc.		exptl.		calc.		exptl.	
E	f*	E	ε†	E	f	E	ε	E	f	E	ε
4,12	0,02	3,94	2730	3,93	0,12	3,94	5000	3,89	0,12	3,90	3370
4,43	0,23	4,59	3670	4,39	0,16	4,70	—	4,32	0,12	4,65	3650
5,67	1,42	5,50	35 640	5,04	1,34	5,15	26 080	5,04	1,18	5,18	31 700
5,84	0,05	—	—	5,56	0,35	5,36	27 530	5,45	0,42	5,30	31 690
5,91	0,51	6,03	39 680	5,99	0,01	—	—	5,70	0,24	5,61	35 325
				6,02	0,95	5,99	38 390	5,96	0,37	5,90	40 520

4-Vinyloxyquinoline (IV)				6-Vinyloxyquinoline (V)				8-Vinyloxyquinoline (VI)			
E	f	E	ε	E	f	E	ε	E	f	E	ε
4,06	0,03	—	—	3,88	0,11	3,93	3700	3,94	0,34	4,06	3980
4,12	0,43	4,50	5900	4,32	0,11	4,65	3840	4,05	0,03	—	—
5,14	0,10	—	—	5,13	1,61	5,27	44 430	5,18	0,25	—	—
5,50	1,02	5,53	39 550	5,45	0,10	—	—	5,36	0,63	5,21	30 660
5,60	0,17	—	—	5,68	0,01	—	—	5,45	0,17	—	—
5,75	0,56	5,64	39 500	6,00	0,45	5,98	34 490	5,90	0,53	6,12	41 630

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*The symbol f indicates the oscillator force.
†The symbol ε indicates the extinction at the maximum of the band.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1662-1665, December, 1977. Original article submitted January 18, 1977.

0009-3122/77/1312-1328$07.50

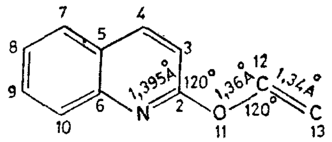

Fig. 1. Geometrical parameters used in the calculation of the vinyloxyquinolines.

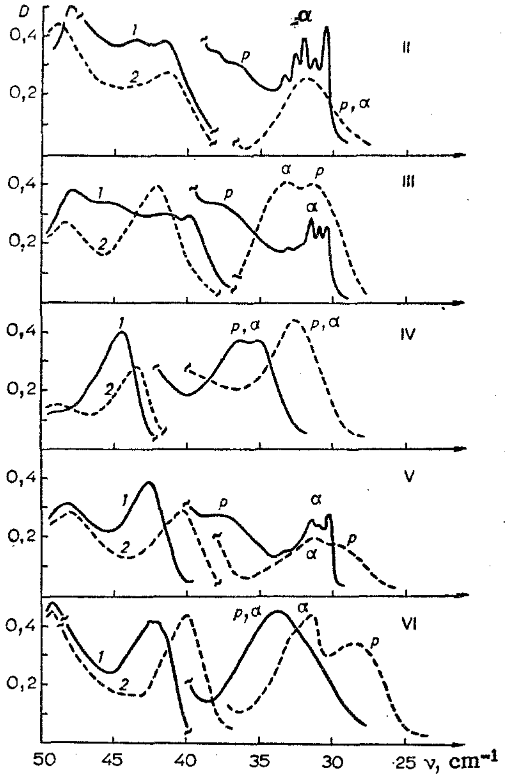

Fig. 2. UV spectra of vinyloxyquinolines: 1) in hexane; 2) in 0.1 N HCl (the numbering is given in Table 2).

$$W_N = -13.5\ \text{eV};\quad W_O = -26.5\ \text{eV};$$
$$\beta_{C=C} = -2.39\ \text{eV};\quad \beta_{C-O} = -2.1\ \text{eV};$$
$$\beta_{C-N} = -2.35\ \text{eV};\quad \beta_{C=C} = -2.92\ \text{eV}.$$

The experimentally determined and calculated energies of the electron transitions of the VOQ are in agreement (Table 1).

The longest-wave band in the electronic absorption spectrum of quinoline is the band due to the transition with an energy of 4.12 eV (the α band [3]). Analysis of the configuration interaction (CI) shows that it corresponds to interaction of the 2 → 1* and 1 → 2* molecular orbitals (MO). The second transition with E = 4.43 eV (the p band) is associated with interaction of the upper occupied and lower vacant MO.

In the case of 2-, 3-, and 6-vinyloxyquinolines there is pronounced mixing of the L_a and L_b states of the corresponding p and α bands. This leads to an increase in the intensity of the α band, during which the oscillator forces of both bands are almost equal. The p band of 2-, 3-, and 6-VOQ is overlapped to a considerable extent by the β band, and the α band has a vibrational structure (Fig. 2).

The transition of 4-vinyloxyquinoline (E = 4.06 eV) corresponds to the L_b state as in the case of quinoline. It is experimentally difficult to identify the α band in the spectrum of 4-vinyloxyquinoline; the increased extinction of the p band (λ = 4.50 eV) and the vibrational structure in its long-wave wing may constitute evidence for its presence.

When the hydrogen atom in the 8 position of the heteroring is replaced by a vinyloxy group, the 1 and 1* MO participate in the transition with E = 3.93 eV. The second transition corresponds to the L_b state. Thus inversion of the $^1A \rightarrow L_a$ and $^1A \rightarrow L_b$ electron transitions is observed in the case of 8-vinyloxyquinoline relative to quinoline itself and its 2-, 3-, 4-, and 6-vinyloxy derivatives. The spectrum of 8-vinyloxyquinoline contains a broad band at ν 34,000 cm^{-1}, which is due to the superimposition of the α and p bands as a result of a bathochromic shift of the latter.

TABLE 2. π Charges ($\Delta\rho$) on the Nitrogen, Oxygen, and Carbon Atoms of the CH_2=CH Group and Integral Intensities ($A_{C=C}^{0.5}$) in Vinyloxyquinolines and Their Hydrochlorides

Substituent position	$\Delta\rho_N$	$\Delta\rho_O$	$\Delta\rho_{C_\alpha}$	$\Delta\rho_{C_\beta}$	$\Delta\Delta\rho_{\alpha,\beta}$	$A_{C=C}$	Hydrochlorides	
							$A_{C=C}$	$\Delta\Delta\rho_{\alpha,\beta}$
2	−0,180	0,172	−0,003	−0,074	−0,071	2826	—	—
3	−0,114	0,163	−0,001	−0,078	−0,077	3044	3478	−0,081
4	−0,151	0,174	−0,003	−0,073	−0,070	2652	870	−0,037
6	−0,122	0,164	0,000	−0,080	−0,080	3304	1261	−0,046
8	−0,128	0,170	0,003	−0,081	−0,084	3783	3913	−0,086

Substitution of quinoline in the 2, 3, and 6 positions gives rise to a change in the form of the MO with local symmetry of the B_{3u} type [4], and the atomic orbitals (AO) of the carbon atoms of the vinyl group participate to a great extent in them. The form of the MO of the B_{3u} type does not change when substituents are introduced in the 4 and 8 positions of quinoline, and the AO of the carbon atoms of the vinyl group make a small contribution to them.

Analysis of the calculated moments of the transitions showed that the L_a and L_b transitions in 4- and 8-vinyloxyquinolines are polarized along the short Y axis. The analogous transitions in 2-, 3-, and 6-vinyloxyquinolines are polarized to a great extent along the long X axis of the molecule. Thus the bathochromic shift of the p band in the spectra of the 4 and 8 derivatives can be explained by an increase in the effect of conjugation along the Y axis of the molecule. Substitution of the vinyloxy group in the 2, 3, and 6 positions of the heteroring affects the α band by increasing the conjugation along the X axis.

The L_a transition is associated to a considerable extent with charge transfer from the substituents to the heterocyclic ring. It has been shown for 8-hydroxyquinoline that this band is shifted to the short-wave region and reversibly on transition of the molecule through the H_2OX^+, HOX, and OX^- states [5]. The energy of the L_b transition does not change in this case.

A pronounced bathochromic shift of the p band is observed in the spectra of the cations of 3-, 4-, 6-, and 8-vinyloxyquinolines (Fig. 2). The smallest shift is observed for 4-vinyloxyquinoline. The position of the bands in the spectrum of 2-vinyloxyquinoline in 0.1 N HCl does not change as compared with the spectra of the compound in neutral solvents. The vinyloxy group in the 2 position of the heteroring evidently hinders the approach of the solvating ion to the nitrogen atom.

In addition to the changes in the character of the MO and the energies of the electron transitions, the presence of a vinyloxy group and its position in the quinoline molecule have a substantial effect on the electron-density distribution in the heterocyclic ring. The charges on the C_α and C_β atoms of the vinyloxy group change simultaneously (Table 2). In a previous study of vinyl aryl ethers it was shown that the integral intensity ($A_{C=C}^{0.5}$) of the band of C=C stretching vibrations in the CH_2=CH–O group is determined by the resonance effect of the substituent and is a linear function of the difference in the charges on the carbon atoms [6]. With the idea of possibly extending this relationship to vinyloxyquinoline systems we measured the intensities ($A_{C=C}$) of the compounds (Table 2). The frequencies of the C=C stretching vibrations in quinolines with different types of substitution lie in a narrow interval (1639-1644 cm^{-1}). We found a linear relationship between the $\Delta\Delta\rho_{\alpha,\beta}^{\pi}$ values and the $A_{C=C}^{0.5}$ values: $A_{C=C}^{0.5} = 642.78\Delta\Delta\rho_{\alpha,\beta}^{\pi} + 6.65$ ($r = 0.98$, and $s = 0.97$). Consequently, the change in the polarity of the C=C bond in vinyloxyquinolines, as in the case of vinyl aryl ethers, is determined principally by conjugation effects.

On the basis of the above conclusion, there is a possibility of estimating the effect of additional substitution from the integral intensities of the vinyl group in vinyloxyquinolines; this becomes very important during the study of their salts. In fact, the reaction with HCl causes a decrease in the intensity of the C=C band in the spectra of 4- and 6-vinyloxyquinolines. The intensity remains unchanged in the spectra of complexes of 3- and 8-vinyloxyquinolines as compared with the intensities in the spectra of the ligands. A formal positive charge on the nitrogen atom is a consequence of salt formation. However, the increase in the positive charge on the oxygen atom and the change in the difference in the charges on the C_α and C_β atoms of the vinyl group depend on the position of the vinyloxy group in the quinoline ring. Thus one observes an analogy between the intramolecular effects in quinolines and the orienting properties of substituents in the benzene molecule: the 3 and 8 positions of the quinoline ring correspond to meta substitution in the benzene ring, while the 4 and 6 positions of quinoline are analogous to para substitution in the benzene ring.

On the basis of the established $A_{C=C}^{0.5} = f(\Delta\Delta\rho_{\alpha,\beta\pi})$ dependence, we estimated the polarity of the vinyloxy group in salts of the investigated compounds: its low value in the case of 4- and 6-vinyloxyquinoline hydrochlorides should correspond to a decrease in the reactivity of the vinyl group with respect to electrophilic reagents.

EXPERIMENTAL

The UV spectra of solutions of the compounds in n-hexane and in 0.1 N HCl at 25,000-50,000 cm^{-1} were obtained with a Specord UV-vis spectrophotometer. The IR spectra of cyclohexane solutions of the vinyloxyquinolines and KBr pellets of their hydrochlorides at 1400-1700 cm^{-1} were obtained with a UR-20 spectrometer. The $A_{C=C}$ integral intensities (on the IUPAC scale) were calculated by the Ioggansen method [7]. The hydrochloride concentrations were calculated by the method in [8]. The synthesis of the investigated compounds is described in [9, 10].

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