AN INTRAMOLECULAR CHARGE-TRANSFER COMPLEX IN HYDROGENATED QUINOLINES

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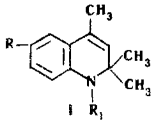
The IR spectra of 6R-2,2,4-trimethyl-1,2-dihydroquinolines (I) and 6R-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines (II) with R = H, CH_3, OCH_3, and OC_2H_5 and those of their acetyl derivatives have been studied. The change in the intensity and the frequencies of the bands of the stretching vibrations of the C—N and C=C bonds and the ring with a change in the structure of the molecule have been considered. The considerable differences in the IR and UV spectra of I and II are explained by the fact that in the I series the interaction between the p-electrons of the nitrogen and the π-electrons of the double bond (of the CTC type) and in the II series that of the ρ-electrons of the nitrogen with the aromatic ring is predominant.

We have previously [1] observed considerable differences in the UV spectra of 6R-2,2,4-trimethyl-1,2-dihydroquinolines (I) and 6R-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines (II), where R = H, CH_3, OCH_3, and OC_2H_5, and R_1 = H.

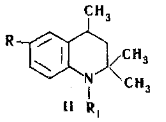
Table 1

Values of λ_{max} and ε_{max} of the K-band in the Electronic Spectra of I and II (R = H), Their Acetyl Derivatives, and Their Cations.

Compound	R_1	λ_{max}	ε_{max}
I	H	232	35400
I	$COCH_3$	244	28000
I	Cation	257	11500
II	H	245	9200
II	$COCH_3$	250	13000
II	Cation	259	1300



I



II

Thus, the intensity of the π → π* electronic transition (K-band) of the derivatives I with R_1 = H is 2–3 times greater than the intensity of the band of the derivatives II with R_1 = H and is shifted slightly in the hypsochromic direction. These differences are still stronger in the spectra of the cations of I and II (R = H) (Table 1).

In the ~260 nm region, a band is observed as an inflection in the long-wave wing of the K-band only for series I (R_1 = H). Its intensity increases by a factor of almost 2 when an alkoxy group is introduced.

At the same time, we have found [1] a considerable bathochromic shift (40–50 nm) and an increase in the intensity of the long-wave B-band which, for nitrogen-containing compounds, is extremely sensitive to a change in the state of the p-electrons of the nitrogen. This difference in the electronic spectra of I and II (R_1 = H) is particularly appreciable for R = H and decreases somewhat for R = C_2H_5O.

The latter circumstance is explained by the fact that in a consideration of the series of derivatives II, with R = H, CH_3, OCH_3, and OC_2H_5, beginning with the unsubstituted tetrahydroquinoline, a small bathochromic shift of the B-band and a hypsochromic shift and an increase in the intensity of the K-band can be found [1]. This general feature appears still more strongly in series I with R_1 = H and probably shows an increase in intramolecular interaction competing with the effect of the conjugation of the p-electrons of the nitrogen with the aromatic ring*.

We have studied the IR spectra of I and II with R_1 = = H and $COCH_3$ and R = H, CH_3, OCH_3, and OC_2H_5. Figs. 1–3 show the form of the spectra of four substances in the 1200–1800 cm^{-1} region. This region is of the greatest interest, since it enables us to follow in the main links in the quinoline ring (the C—N, C=C, and ring vibrations) with a change in the structure of the molecule. We have considered the region of the N—H stretching vibrations previously [2].

There is an extremely limited amount of information on the assignment of the absorption bands in the spectra of hydrogenated heterocycles [3]. However, for the 1500–1700 cm^{-1} region this assignment can be carried out fairly unambiguously. For the structure I with R_1 = H, four bands are found in this region, three at about 1600 cm^{-1} and one at about 1500 cm^{-1}. Bands at 1600 cm^{-1} (ν_1) and 1500 cm^{-1} are found with many nitrogen-containing heterocycles and characterize the stretching vibrations of the ring. The band at ~1640

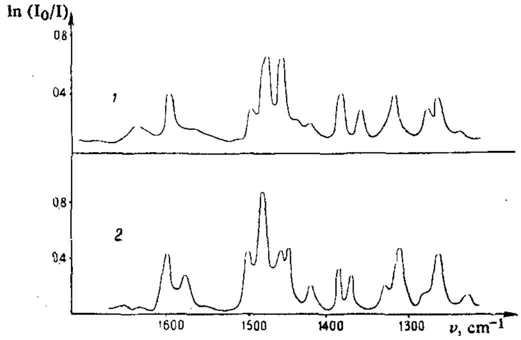


Fig. 1. IR absorption spectra: 1) I, R_1 = R = H; 2) II, R_1 = R = H.

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*An intramolecular CTC between the p-electrons of the nitrogen and the π- or σ-bond in position 4 of the hydrogenated ring is possible.

cm^{-1} is due to the stretching vibrations of the C=C bond in the partially hydrogenated pyridine ring of quinoline. This band is absent from the spectra of compounds II (R_1 = H, $COCH_3$).

Information relating to the 1550–1600 cm^{-1} band (ν_2) is fairly contradictory. It is assigned [4–6] either to weak ring vibrations, which do not always appear, or to external C—N—H deformation vibrations for secondary amines. The latter is unlikely in our case, since an analogous band is found for the acetyl derivatives I and II. The spectral parameters of the bands of structures I and II (R_1 = H) are given in Table 2. The figures given indicate a small change in the frequencies, which are practically the same for all the compounds and are within the limits of experimental error. An exception is the band of the C—N vibrations considered below. Attention is attracted by the intensity of the aromatic ε_1 and ε_2 bands.

The band at 1600 cm^{-1} is not sensitive to the presence of an ethylenic bond. Its intensity is low, both in I and II, in agreement with the decrease in the difference of the σ constants of the substituent R and the N—H group. On the other hand, in the I and II series the ε_1 intensities of derivatives with the same R are found to be equal. This indicates the absence of any appreciable conjugation between the ring and the ethylenic bond in the I derivatives, which is confirmed by the fairly high value of its frequency, a characteristic of isolated C=C bonds.

Conversely, the band at ~1570 cm^{-1} is sensitive to the presence of an ethylenic bond, and its intensity ε_2 changes differently for I and II.

In the first case, substituents have the opposite effect: alkoxy groups increase its intensity as compared with R = H and CH_3, i.e., their action is opposite to their action on the 1600 cm^{-1} bond. In the second case, in the II derivatives, this effect is less clear and is rather a compromise effect.

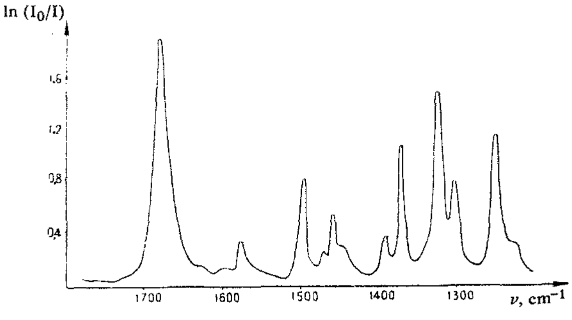

Fig. 2. IR absorption spectrum of I, R_1 = = $COCH_3$, R = H.

The possibility is not excluded that the aromatic band at 1570 cm^{-1} reflects the influence of an intramolecular CTC between the ortho substituents (N—H—π-bond) in the vibrations of the aromatic ring.

The intensity of the ethylenic bond also corresponds to some degree to the polar nature of the substituent and changes symbatically with the aromatic band at 1600 cm^{-1}.

The decrease in the intensity of the $\nu_{C=C}$ and ν_1 bands observed in the IR spectra of I and II can also be explained by some increase in the symmetry of the molecule with the introduction of an alkoxy group.

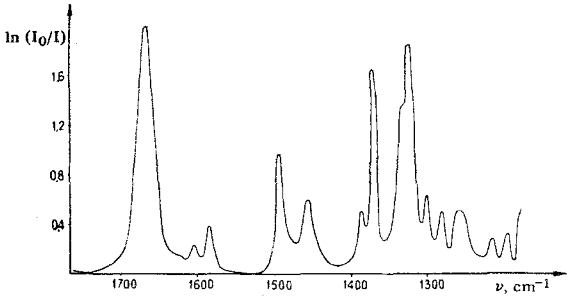

Fig. 3. IR absorption spectrum of II, R_1 = = $COCH_3$, R = H.

In the IR spectra of the acetyl derivatives I and II (R = H, R_1 = $COCH_3$) a strong band with the stretching vibrations of the C=O group appears which is very sensitive to a minute change in the degree of double-bondedness of the carbonyl with a change in the conjugation effect.

In comparing the spectra a small but appreciable rise in the $\nu_{C=C}$ frequency (1680 cm^{-1}) for I with R = = H can be seen (for II with R = H, $\nu_{C=C}$ = 1666 cm^{-1}) which indicates a weakening of the interaction of the C=O group with the unshared pair of electrons of the nitrogen atom. This is evidently due to the stronger competing intramolecular effect. If this effect were an enhancement of the conjugation of the p-electrons with the ring, the intensity of the vibrations of the ring in the acetyl derivatives I would increase in comparison with the derivatives II (general influence of the conjugation effect). In practice, however, the intensities of these bands in I are almost equal (ε_1 = 151) or even somewhat lower than in II (ε_1 = 211).

A considerable difference between the acetyl derivatives I and II can also be seen from the features of the electronic spectra (Table 1). For II with R = H, the introduction of a $COCH_3$ group leads to the general effect of the elongation of the chain of conjugation: ring — p-electrons of the nitrogem atom —C=O group (whereupon the value of λ_{max} and ε increase somewhat). For I with R = H, a fall in the intensity of the K band with a bathochromic shift is found, probably because of a partial decrease in the intramolecular interactions with the introduction of a $COCH_3$ group.

The spectroscopic effects considered are completely analogous to the changes found in a series of compounds with intramolecular interaction through a field [7].

Of great interest in connection with the effect considered earlier is the region of the C—N stretching vibrations which, however, is difficult to interpret and has been studied even less for hydrogenated heterocycles than the region of the C=C vibrations. There is much evidence that there are two bands in the region of $\nu_{C—N}$ of aromatic amines: 1360–1250 and 1280–1180 cm^{-1} (analogous to $\nu_{C—N}$ in aliphatic amines) [3, 5, 6]. For heterocyclic amines the existence of three $\nu_{C—N}$ bands in this region is possible (1319, 1299, and 1240 cm^{-1}) [8].

Table 2

Frequencies and Intensities of the Absorption Bands in the IR Spectra of I and II (R_1 = H)

Compound	R	C=C			Ring			Ring			C—N	
		ν, cm^{-1}	ε	$A \cdot 10^{-4}$	ν, cm^{-1}	ε_1	$A_1 \cdot 10^{-4}$	ν_2, см$^{-1}$	ε_2	$A_2 \cdot 10^{-4}$	ν, cm^{-1}	ε
I	H	1639	93	0.30	1597	205	0.58	1571	71	—	1317	250
II	H	—	—	—	1597	215	0.65	1573	131	0.34	1310	300
I	CH_3	1640	94	0.23	1605	94	0.28	1573	68	0.28	1311	272
II	CH_3	—	—	—	1608	101	0.33	1573	30	—	1309	293
I	OCH_3	1641	56	0.13	1604	53	—	1570	151	0.44	1309	258
II	OCH_3	—	—	—	1603	36	—	1572	88	0.30	1293	200
I	OC_2H_5	1638	56	0.14	1606	52	—	1575	135	0.40	1301	263
II	OC_2H_5	—	—	—	1600	44	—	1570	76	0.27	1299	225

We have found two strong bands at about 1300–1320 and 1260 cm^{-1}, the intensity and position of which vary in all the intramolecular processes connected with the nitrogen. It is characteristic that when an alkoxy group is introduced into I or II a small increase (Table 1) is observed in the frequency of the shortwave ν_{C-N} band at 1320–1300 cm^{-1}, evidently in agreement with the weakening of the conjugation of the ρ-electrons of the nitrogen atom and the ring. In view of the partial overlapping of the vibrations of the alkoxy groups, the change in the second ν_{C-N} band is not always clear.

Since the only difference between series I and II is the presence of an ethylenic bond in the hydrogenated pyridine ring of the quinoline, it is natural to assume (on the basis of all the spectroscopic effects discussed) that in series I a spatial intramolecular interaction between the π-electrons of the cloud of the double bond and the p-electrons of the nitrogen is predominant.

In series II, particularly with R = H (as with the arylamines), the interaction of the p-electrons of the nitrogen with the π-electrons of the aromatic ring is possible to a greater extent than in I.

EXPERIMENTAL

The IR spectra were recorded on UR-10 and IKS-14 spectrophotometers with NaCl prisms (solutions in CCl_4, c = 0.05–0.1 mole/l, l = 0.1 mm). The recording of the I_0 line was carried out with the solvent in both cells. The integral intensities of the IR bands (A, l/mole^{-1} · cm^{-2}) were determined by Ramsay's method [9]. The UV spectra were obtained on an SF-4A spectrophotometer (solutions in propanol, c = = 0.01–0.001 mole/l, l = 0.1 mm). The peak intensities of the UV and IR bands were defined as $\varepsilon = [\ln (I_0/I)]/cl$ l/mole^{-1} · cm^{-1}.

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