A STUDY OF HETEROCYCLIC QUINONES X*. STRUCTURE AND IR SPECTRA OF QUINOLINE-5,6-QUINONES SUBSTITUTED IN POSITION 4

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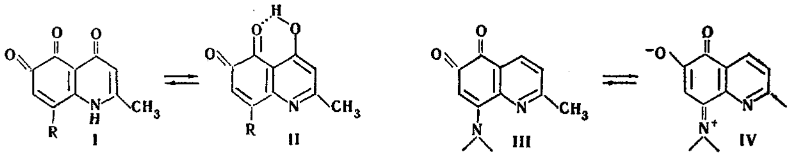
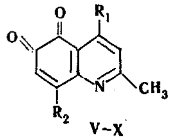
By studying their IR spectra it has been shown that in the solid state and in solutions 4-hydroxyquinoline-5,6-quinones exist in the hydroxy form stabilized by a strong intramolecular hydrogen bond.

It has been shown by physicochemical methods that in the solid state quinol-4-ones exist in the oxo form [1] and in solution (water) the equilibrium is likewise displaced in the direction of the oxo form, the oxo : hydroxy ratio being ~10^4 [2]. It has recently been established that some esters of 2-alkylthio-4-oxoquinoline-3-carboxylic acids can be obtained in the forms – hydroxy and oxo – between which tautomeric relationships exist [3].

In a study of 4-oxo derivatives of quinoline-5,6-quinones, we directed our attention to their capacity for forming stable complexes with copper salts which decompose only under the action of strong acids [4]. This can easily be explained if it is assumed that they exist in the hydroxy from II stabilized by a strong intramolecular hydrogen bond. To confirm the structure of these compounds, we studied the IR spectra of quinoline-5,6-quinones substituted in position 4 in the solid state and in solutions.





V–X

V R_1 = Cl, R_2 = H; VI R_1 = H, R_2 = NC_5H_{10}; VII R_1 = R_2 = NC_5H_{10}; VIII R_1 = NH_2, R_2 = NC_5H_{10}; IX R_1 = OH, R_2 = NC_5H_{10}; X R_1 = OH, R_2 = $N(CH_3)_2$

The IR spectra of solid samples of 4-hydroxyquinoline-5,6-quinones (IX and X) in paraffin oil have a broad band of medium intensity in the 3000 cm^{-1} region which cannot be unambiguously assigned to an associated ν_{O-H} or ν_{N-H}. For the oxo form I in dilute solutions the appearance of the band of a free N–H group at 3442 cm^{-1} was to be expected [5]. However, dilute solutions of compounds IX and X in carbon tetrachloride (concn. 0.0035 M, 1.2 mm cell) show only a broad weak band in the 3200-2500 cm^{-1} region which is characteristic for a strong intramolecular hydrogen bond [6]. The absence of N–H absorption is in favor of the hydroxy form (II) but does not permit a definitive conclusion on the structure of the quinones IX and X. Consequently, our main attention was devoted to the absorption in the 1700-1500 cm^{-1} region. In order to assign the bands in this region, the spectra of 4-hydroxy-quinoline-5,6-quinones were compared with the spectra of quinolinequinones containing on the C_4 atom hydrogen (VI), chlorine (V), a piperidine

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*For Communication IX, see [11].

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TABLE 1. Main Absorption Bands of Quinoline-5,6-quinones in the 1700-1200 cm^{-1} Region in Paraffin Oil.

Compound	$\nu_{C_5=O}$	$\nu_{C_6=O}$	$\nu_{C=C}$	$\nu_{C=C}$	$\nu_{C=N}$	$\nu_{C=C}$	δ_{O-H}	δ_{C-H}*	ν_{C-O}
V	1701	1680	1650	1616	1568	1530	—	1380	—
VI	1690	1622	1592	1569	1551	1455	—	1370	—
VII	1678	1620	1590	1560	1551	1460	—	1370	—
VIII†	1658	1621	1608	1582	1558	1460	—	1370	—
IX	1650	1626	1603	1570	1550	1450	1405	1370	1215
X	1650	1620	1600	1573	1551	1460	1400	1370	1210

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*There is also a band in this region in the spectra measured in chloroform:

† In chloroform (concn. 0.001 M, 1-mm cell).

TABLE 2. Influence of the Solvent on the Absorption of the Quinones VI and IX in the 1700-1500 cm^{-1} Region.

Solvent	VI					IX				
	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C=C}$	$\nu_{C_6=O}$	$\nu_{C_5=O}$	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C=C}$	$\nu_{C_6=O}$	$\nu_{C_5=O}$
CCl_4	—	—	—	1636	1708	—	—	—	1638	1670
Dioxane	1555	1574	1596	1634	1706	1557	1570	1605	1635	1670
Dichloroethane	1550	1573	1600	1618	1701	1551	1570	1608	1623	1659
Chloroform	1550	1572	1604	1613	1700	1552	1570	1603	1622	1658
Bromoform	1550	1570	1608*		1700	1549	1572	1603	1618	1658
Methylene iodide	1555	1570	1600	1611	1697	1548	1572	1603	1615	1654
$\Delta\nu$	5	4	8	25	11	9	2	5	23	16

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* Center of a broad band.

residue (VII), or an amino group (VIII), which should have an influence on $\nu_{C_5=O}$ similar to the influence of a hydroxy group.

In the spectrum of compound V there are two carbonyl maxima, at 1701 and 1680 cm^{-1} (Table 1). In compounds VI and VII, the nature of the absorption in this region changes. Of the five bands between 1700 and 1500 cm^{-1} only one can reliably be assigned to $\nu_{C=O}$: with maxima at 1690 cm^{-1} for VI and 1678 cm^{-1} for VII. These bands were assigned to the $\nu_{C_5=O}$ absorption since, in the quinones containing a nitrogen atom at C_8 (III) a displacement of the carbonyl absorption $\nu_{C_6=O}$ in the long-wave direction was to be expected because of the contribution of structure IV. The ring nitrogen atom cannot have this influence on $\nu_{C_5=O}$.

In the spectrum of compound VIII the $\nu_{C_5=O}$ band (1658 cm^{-1}) is shifted considerably in the long-wave direction through the formation of an intramolecular hydrogen bond. In order to exclude intermolecular hydrogen bonds and their influence on $\nu_{C_6=O}$ the spectrum of this compound was taken in dilute chloroform solution at a concentration of 0.001 M. The same pronounced shift of the $\nu_{C_5=O}$ band is found in the quinones IX and X as compared with VI (Table 1). The low frequency of $\nu_{C_5=O}$ in these compounds is also due to the presence of an intramolecular hydrogen bond, which is possible only if IX and X exist in the hydroxy form.

In order to assign the absorption bands in the 1620-1550 cm^{-1} region, the spectra of the quinones VI and IX were taken in solvents of different polarities (Table 2). This method has been used successfully to establish the structure and study the carbonyl absorption of pyridines [7] and 4-hydroxycarbostyryls [8]. It can be seen from Table 2 that "acid" solvents [9] exert the greatest influence on the two bands both in VI ($\Delta\nu$ 25 cm^{-1} and 11 cm^{-1}) and in IX ($\Delta\nu$ 23 cm^{-1} and 16 cm^{-1}). One of them is ascribed to $\nu_{C_5=O}$ and the second corresponds to $\nu_{C_6=O}$. As was to be expected, $\nu_{C_6=O}$ (1636 cm^{-1} in carbon tetrachloride) for the quinone VI undergoes practically no change on passing to IX. Attention is attracted by the fact that the frequency of the carbonyl conjugated with the exocyclic nitrogen or participating in the formation of a hydrogen bond is more sensitive to a change in the polarity of the solvent. The assignment of $\nu_{C=C}$ and $\nu_{C=N}$ was made by analogy with known compounds. Finally, the spectra of the quinones IX and X have bands at about 1400 and 1200 cm^{-1}. These bands are absent from the spectra of compounds V-VIII and we assign them to δ_{O-H} and ν_{C-O} of the hydroxy group on the basis of available correlations [6] and by analogy with [3].

Thus, it has been shown that 4-oxo derivatives of quinoline-5,6-quinones exist in the stable hydroxy form, stabilized by a strong intramolecular hydrogen bond.

EXPERIMENTAL

All the compounds studied have been described by previous papers [4,10,11]. The spectra were taken on a UR-20 spectrophotometer (Zeiss). The spectra of compounds V-X were recorded in paraffin oil (Table 1) and those of compounds VI and IX in various solvents (concentration 0.01 M, 0.60-mm cell).

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