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SPECTRA AND STRUCTURE OF SALTS OF N-METHYLQUINOLONES

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The structures of salts of N-methylquinol-2- and -4-one are considered, using their IR spectra. It is shown that formation of salts from N-methylquinolones is accompanied by protonation of the carbonyl group. The problem of relating the 1500–1700 cm^{-1} band in the IR spectrum of N-methylquinol-4-one is considered.

The problem of the structure of salts of 2- and 4-pyridones has been under discussion up to the present time. Cations of those compounds can arise by O or N protonation. From IR and Raman spectra data, Spinner [1] concluded that 2- and 4-pyridones were N-protonated. However, a number of subsequent papers showed [2–5], using IR and NMR spectra, that protonation of the carbonyl group is involved in cation formation. In this connection, it was of interest to consider the structure of derivatives of quinol-2- and -4-one.

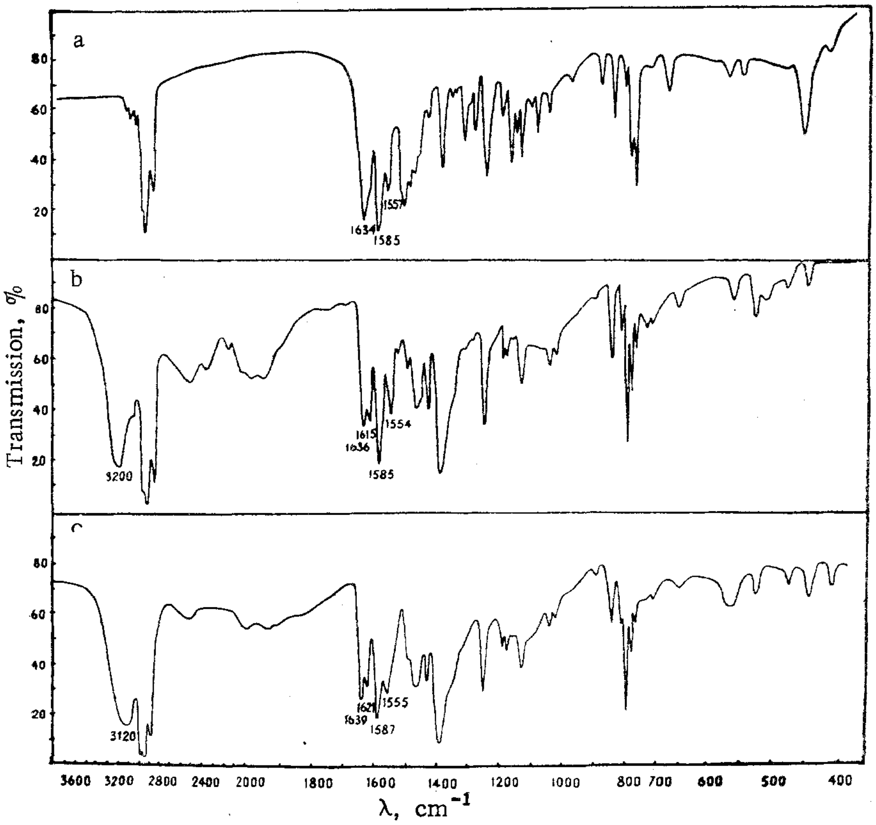
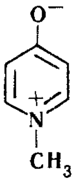
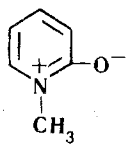


Fig. 1. IR spectra: a) 1-methylquinol-4-one; b) hydrobromide of same; c) hydrochloride of same.

A characteristic peculiarity of the compounds investigated is the partly aromatic character of the pyridone ring, and its tendency to more complete aromatization [6, 7]. This tendency is manifest in the tendency to form a stable aromatic configuration of mobile electrons, in accordance with Hückel's rule (from 6 electrons for pyridones and 10 for quinolones), which must be accompanied by formation of bipolar ions of types I and II.



I

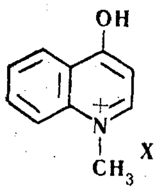


II

Hence it is to be expected that, in salt formation, the proton will add, not to the nitrogen atom, but to the oxygen of the carbonyl group.

Due to the negative inductive effect of the neighboring nitrogen atom, the electron density at the oxygen atom must be less in the case of the α isomer than for the γ one. In particular, this is manifest in the smaller pK_a value for pyrid-2-one, than for pyrid-4-one, (respectively, 0.8 and 3.3).

Our data for salts of 1-methylquinol-4-one and 1,4-dimethylquinol-2-one are in accord with these views. Actually, the IR spectra of 1-methylquinol-4-one hydrobromide and hydrochloride (Fig. 1) exhibit strong hydroxyl bands at 3200 and 3120 cm^{-1}, respectively, which indicate structure III, and not IV. Furthermore, the carbonyl band for compound IV should lie in a region of higher frequencies in comparison with its position in the case of 1-methylquinol-4-one, due to the electron-accepting action of the positively charged nitrogen atom. The spectra of the salts investigated do not, however, show a shift of bands in the 1500–1700 cm^{-1} region, in the direction of higher frequencies. At the same time, in structure III, the positively charged nitrogen atom affects the hydroxyl in such a way that it becomes more acid, and more readily forms hydrogen bonds. To this is due both the rather low position of its frequency, and the presence of a number of bands in the 1900–2800 cm^{-1} region, which probably relate to hydroxyl groups hydrogen bonded to the halogen atom.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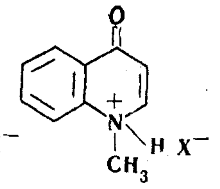
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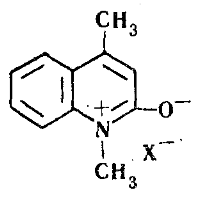
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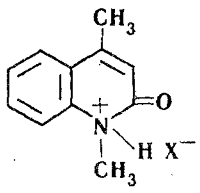

VI

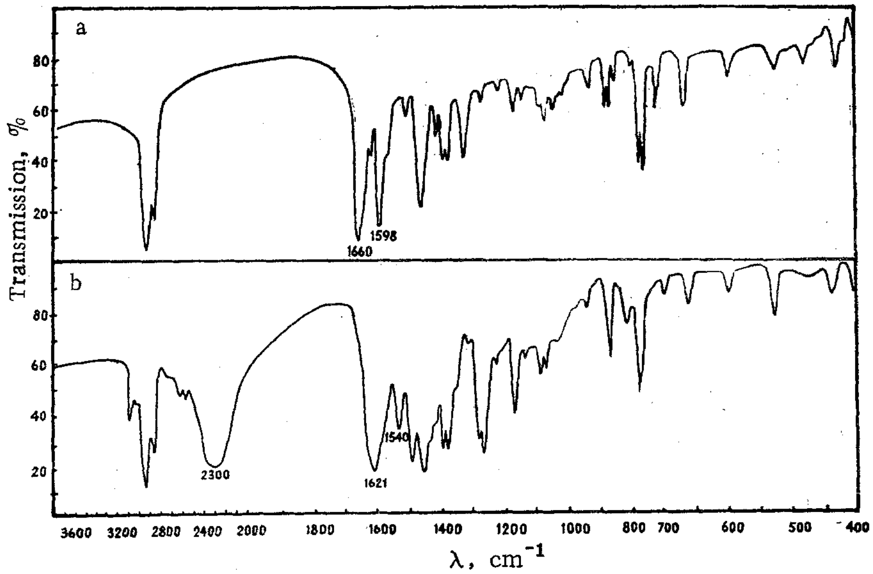
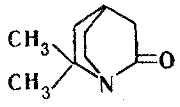


Fig. 2. IR spectra: a) 1,4-dimethylquinol-2-one; b) hydrobromide of same.

A similar picture also obtains for a salt of 1,4-dimethylquinol-2-one. There the hydroxyl band lies substantially lower, at about 2300 cm^{-1}, which is connected with a more powerful effect of the positively charged nitrogen atom, at the α position.

The positions of the absorption bands in the region of C=O and C=C valence vibrations are also in accord with formula V for the salt investigated. The spectrum of the hydrobromide contains, in place of a strong C=O group band (1660 cm^{-1}) band, and bands at 1623, 1598, and 1577 cm^{-1}, due to vibrations of the ring of the initial base, bands at 1621 and 1540 cm^{-1}, obviously related to vibrations of the ring in structure V. Were formula VI correct, a carbonyl band lying at about 1780–1800 cm^{-1} ought to be present, e.g., as with 2, 2-dimethylquinuclid-6-one hydrochloride (VII) (1799 cm^{-1}) [8].



VII

Thus salt formation from quinol-2- and 4-one involves carbonyl group protonation.

Review of the spectra of 1-methylquinol-4-one salts enables some conclusions to be drawn regarding bands in the 1500–1700 cm^{-1} region. Usually a band near 1650 cm^{-1} in the spectra of pyridines and quinol-4-ones belongs to carbonyl group vibrations [9–11], and the band at 1570–1600 cm^{-1} to ring vibrations. A number of authors [4, 5, 12] have criticized this assignment for pyridones, and they assigned the high frequency band to ring vibrations, and the low frequency one to C=O vibrations.

Thus, definite interest attaches to comparison of spectra of 1-methylquinol-4-one with those of its salts with a view to determining how salt formation affects each of these bands. Figure 1 shows that, on passing from base to salts, the 1557 and 1585 cm^{-1} bands stay practically unaltered, while the 1634 cm^{-1} band splits into two components, 1636–1639 cm^{-1} and 1615–1621 cm^{-1}. Here, the intensity of the doublet in comparison with the 1585 cm^{-1} band is somewhat less, than the intensity of the 1634 cm^{-1} band in the spectrum of the base. These data indicate full assignment of the high frequency band to C=O group vibrations. Probably in actual fact there is strong interaction between ring vibrations and those of the carbonyl group, since a contribution from both types of vibration enters each of these bands.

Experimental

1-Methylquinol-4-one. This was isolated from globe-thistle seeds. After recrystallizing from EtOH and vacuum-drying it had mp 151–152° C.

1-Methylquinol-4-one hydrochloride. Prepared by mixing EtOH solution of the base with an ethereal solution of HCl, and repeatedly recrystallizing from EtOH-ether. After vacuum-drying it had mp 193–195° C. Found: C 61.54, 61.39; H 5.15, 5.19; N 7.09, 7.17; Cl 17.85, 17.59%. Calculated for $C_{10}H_9NO \cdot HCl$: C 61.39; H 5.11; N 7.16; Cl 18.15%.

1-Methylquinol-4-one hydrobromide. Prepared by adding a small portion of ether, saturated with HBr, to the ethanolic solution of the base. The precipitate which separated as large crystals was filtered using a water-pump vacuum, washed with dry ether and recyrstalized from EtOH. After vacuum-drying, mp 188–189°. Found: C 50.21; 50.28; H 4.54; 4.45; N 5.76; 5.68; Br 33.01; 32.91%. Calculated for $C_{10}H_9NO \cdot HBr$: C 50.00; H 4.17; N 5.83; Br 33.30%. After repeated recrystallization from EtOH and vacuum-drying, 1,4-dimethylquinol-2-one, mp 132-133°.

1,4-Dimethylquinol-2-one: Prepared in the manner described for 1-methylquinol-4-one hydrobromide.

The spectra were measured with a UR-10 spectrophotometer. The compounds were investigated as pastes in vaseline.

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