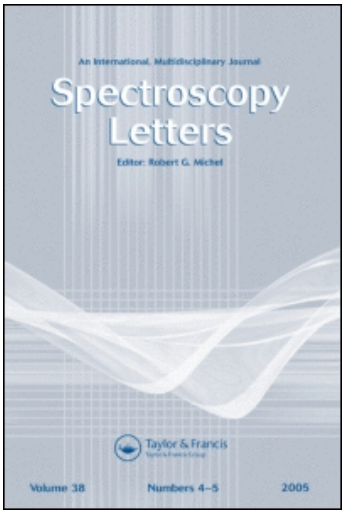

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Infrared Spectral Studies of Quinoline-N-Oxides and Isoquinoline-N-Oxides

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INFRARED SPECTRAL STUDIES OF QUINOLINE-N-OXIDES AND ISOQUINOLINE-N-OXIDES

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The infrared characteristics of aromatic-N-oxides and their correlations with other structural properties have been investigated in some details in monocyclic compounds, especially pyridine-N-oxides. However the amount of infrared observational data available in more complex systems is rather limited and its interpretation still mostly tentative (1).

In the present work, which is mainly concerned with the spectral features related to the presence of the N→O group in quinoline-N-oxides and isoquinoline-N-oxides, the spectra of several derivatives were examined and compared with those of the corresponding quinolines and isoquinolines. For a better understanding of the infrared behaviour of the N→O group, some heptadeuterated compounds were also analyzed.

EXPERIMENTAL

Quinoline-N-oxides and isoquinoline-N-oxides were usually obtained from the corresponding quinolines and isoquinolines (products commercially available or prepared by standard methods) by oxidation with H_2O_2 in acetic acid (2); only for obtaining 2-Chloro-quinoline-N-oxide, monopermaleic acid was used (3). 4-Methoxy-quinoline-N-oxide was prepared from 4-Chloro-quinoline-

-N-oxide by replacement (4). Quinoline-N-oxide-d-7 and isoquinoline-N-oxide--d-7 were obtained by hydrogen-deuterium exchange in the presence of acidic and basic catalyst following the results of an investigation of Kawazoe and Ohnishi (5). Quinoline-d-7 was prepared by reduction with PCl_3 of quinoline--N-oxide-d-7. Isoquinoline-d-7 could not be obtained. All the samples were purified by sublimation in vacuum and/or recrystallization; their melting points and other physical properties agreed well with published values. Care was taken in handling these compounds which are known to be very hygroscopic. Before recording each spectrum, the region 3650-3100 cm^{-1} was checked; only samples, in which no absorption due to water was detected, were used.

The infrared measurements were carried out on a Perkin-Elmer 225 Spectrophotometer (1.0 mm. matched cells) by using C_2Cl_4 and CS_2 as solvents. In most of the cases saturated solutions were employed. The frequency values are given within ±1 cm^{-1}, while the $\Delta\nu_{OH}$ measurements appear to be accurate to ±6 cm^{-1}. The absorption of CH_3OH in the range 1400-1100 cm^{-1} (when ternary solutions were employed) was extinguished by compensation in the solvent cell.

RESULTS AND DISCUSSION

As known (1), the N→O stretching vibration of pyridine-N-oxides appears in the infrared (1200-1300 cm^{-1}) as a very strong band, which shifts toward lower frequencies (20-40 cm^{-1}) by addition of methanol (1,6). In quinoline--N-oxides, however, this vibrational mode has not been clearly assigned yet, but only the presence of two or more bands in the range 1150-1350 cm^{-1} has been pointed out as typical of all of these compounds (7,8).

Since quinoline-N-oxide (isoquinoline-N-oxide) differs from quinoline (isoquinoline) only by an extra N→O bond, while the rings are not modified, many of the vibrational frequencies of the former compound can be expected to be very close to those of the latter one. The vibrational frequencies of

quinoline and isoquinoline were recently investigated by Wait and McNerney (9) mainly by comparison with those of naphtalene, for which reasonable results of normal coordinate analyses are available (10,11,12). It follows that an examination of the sequence naphtalene/quinoline (isoquinoline)/ quinoline-N-oxide (isoquinoline-N-oxide) should be useful for the interpretation of the vibrational bands of the compounds here investigated. The same trend is obviously expected for the corresponding heptadeuterated compounds.

As most of the present interest is confined on the N→O stretching vibration, the range of investigation as in pyridine-N-oxides (6) was limited between 1000 and 1400 cm^{-1}.

Infrared spectra of quinoline-N-oxide: In table 1 the frequency values of the following couple of compounds (naphtalene/naphtalene-d-8, quinoline/quinoline-d-7, quinoline-N-oxide/quinoline-N-oxide-d-7) were listed also by using an empirical approach of Lippincott and O'Reilly (11). From the same table the existence of a good correspondence both between the spectra of the hydrogenated and deuterated terms and the spectra of quinoline-bases and the corresponding N-oxides can be pointed out.

Two strong absorptions at 1233 cm^{-1} and at 1307 cm^{-1} in quinoline-N-oxide appear of some interest. The band at 1233 cm^{-1} has been attributed here to the N→O stretching vibration: in fact, (i) there is no significant absorption in the same spectral region of quinoline (a very weak band observed in liquid by Wait and McNerney was assigned by these authors to a combination mode (9)) and (ii) this is the only band in this spectral range which appears to interact with methanol ($\Delta\nu$=5 cm^{-1}). The band at 1307 has been related to the absorption at 1316 cm^{-1} in the spectrum of quinoline which was assigned to a vibrational motion mainly involving the CN bond (9); the small shift and the enhancement in intensity observed in quinoline-N--oxide can be accounted for to an electronic perturbation on the CN bond

TABLE 1

Comparison of assigned frequencies (cm^{-1}) for naphtalene, quinoline (isoquinoline), quinoline-N-oxide (isoquinoline-N-oxide), and their heptadeuterated derivatives.

ass.[1]	Naphtalene[2]		Quinoline		Quinoline N-oxide		Isoquinoline	Isoquinoline N-oxide	
	h-8	d-8	h-7	d-7	h-7	d-7	h-7	h-7	d-7
ν_{11}	1509	1385	1500s	1382w	1509s	§	1498s	1492w	1373s
ν_{12}	1460	1381	1468w	1365w	1445m	1347m	1458w	1450s	1348w
ν_{13}	1436	1330	1431m	1303m	1440m	1308m	1430w		1315w
ν_{14}	1389	1260	1393m	1257m 1237m	1393s	1230m	1382m	1378w	1250m
ν_{15}	1379	1293	1375s	1288m	1370w	§	1375m	1368w	1287w
ν_{16}	1361	1318	1316m	1280s	1307s	1330s	1315w	1323s	1330s
ν_{17}	1265	1037	1261w	1033s	1267s	1025m	1271s	1276s	1032m
$\nu N \rightarrow O$					1233s	1184s		1183s	1211s
ν_{18}	1209	1082	1217m	1089s	1213m	1070w	1250m	1254s	1132w
ν_{19}	1240	1030	1190w	1010w	1176m	1010m	1175w	1174w	992m
ν_{20}	1144	866	1141m	887s	1142m	872s	1139m	1144w	905w
ν_{21}	1125	885	1119s	870s	1135s		1119w	1126s	881m
ν_{22}	1168	929	1094w	§	1089m	§	1095w	§	§
ν_{23}	1025	835	1033s	830m	1054w	840m	1034m	§	§
ν_{24}	1008	828	1016m	820s	1013m	820m	1011m	1015w	824w
				1068m[3]		1192m[3]			1260m[3]

§ Not found, probably too weak to be detected.

[1] The assignments for quinoline-h-7, isoquinoline-h-7 and naphtalene-h-8 are taken from ref. (9).

[2] Taken from ref. (10).

[3] Unassigned bands observed in the spectra.

caused by the N→O group. By deuteration the band at 1233 cm^{-1} in quinoline--N-oxide (described as ν_{NO}) moves to 1184 cm^{-1} while its hydrogen bonding sensitivity increases ($\Delta\nu$=14 cm^{-1}). The occurence of a shift of about 50 cm^{-1} by hydrogen-deuterium substitution is obviously related to a strong vibrational interaction between the N→O stretching frequency and C-H and/or C-D in-plane bending modes and may take account for the anomalous behaviour of the N→O vibration in these compounds (see below). Incidentally it may be mentioned here that the N→O stretching frequencies of pyridine-N-oxide-h-7 (1265 cm^{-1}) and pyridine-N-oxide-d-7 (1224 cm^{-1}) (6) are far apart by about 40 cm^{-1}, although the partecipation of modes other than the N→O stretching has been considered not very important here (1). The band at 1307 cm^{-1} moves to 1330 cm^{-1} in quinoline-N-oxide-d-7. It seems peculiar that only in this compound it is sensitive to the addition of methanol ($\Delta\nu$=6 cm^{-1}); some partecipation of the N→O stretching vibration in such vibrational mode is probably involved here.

In figure 1 are shown, in schematic form, the spectra of several ring-substituted quinoline-N-oxides; for comparing, each of those is placed right above that of the analogous quinoline: a good correspondence is usually presented. Particularly, the spectral features observed for the bands of the parent compound at 1233 cm^{-1} and 1307 cm^{-1} are clearly exhibited also by the substituted derivatives. Their frequency range is 1200-1240 cm^{-1} and 1300-1340 cm^{-1} respectively; as expected these bands do not show any correlation with the position and the electronic nature of the substituents.

Infrared spectra of isoquinoline-N-oxides: In table 1 are also reported the infrared bands of isoquinoline-h-7, isoquinoline-N-oxide-h-7 and isoquinoline-N-oxide-d-7. As in the previous section, the assignments for isoquinoline-h-7 refer to the work of Wait and McNerney (9). Probably the most relevant result achieved here is that the two characteristic strong bands already seen in quinoline-N-oxides are also present in the spectrum of isoqui-

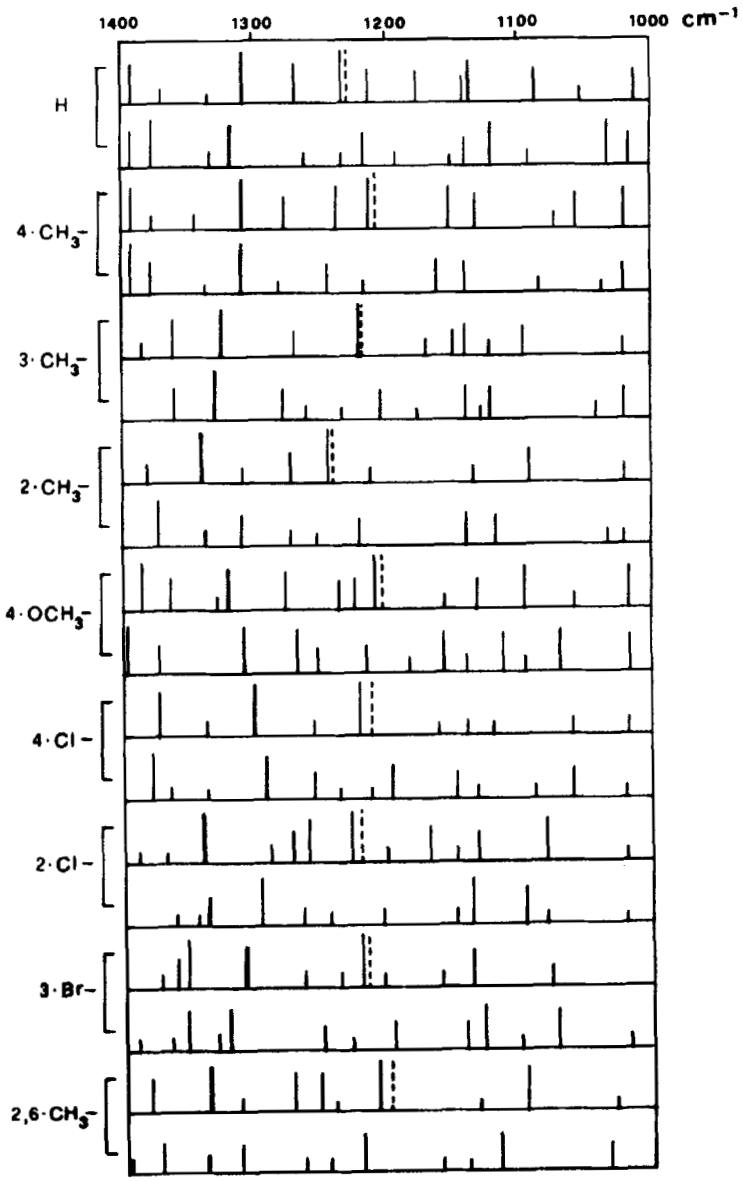

FIG. 1

Position and Relative Intensity of Absorption Bands of Substituted Quinolines and Quinoline-N-oxides in the Range 1400-1000 cm^{-1}. For each couple the spectrum of quinoline-N-oxide lies right above that of the corresponding quinoline. Dotted lines represent the shifts of the N→O band in the presence of CH_3OH; thicker lines represent the band at about 1300 cm^{-1} (see text).

noline-N-oxide. They absorb at 1183 cm^{-1} and 1323 cm^{-1} respectively. Since only the band at lower frequencies is sensitive to the methanol ($\Delta\nu$=10 cm^{-1}), its attribution to the N→O stretching vibration can be easily deduced. Again it is of interest to note that by deuteration the two bands absorb respectively at 1211 cm^{-1} and 1330 cm^{-1} (the possibility of a misassignment appears rather scarce since only the first band is affected by the hydrogen bonding formation ($\Delta\nu$=16 cm^{-1}). It is rather unexpected that by deuteration the N→O vibration moves toward higher wave numbers; in fact this is just the opposite of the trend observed in quinoline-N-oxide and in pyridine-N-oxide. A coupling between the N→O stretching frequency and some vibrational motions other than in the latter compounds is probably responsible for such effect. This is a further example of the complexity of the vibrational interactions which take place on quinoline- and isoquinoline-N-oxides.

The results of figure 2, where are drawn the spectra of few ring-substituted isoquinoline-N-oxides compared with those of the corresponding isoquinolines, appear to clearly support the existence of the two characteristic absorptions.

Hydrogen bonding interaction with methanol: It is well established that the magnitude of the shift $\Delta\nu_{OH}$ between the free and the bonded hydroxylic stretching vibration provides a measure of the strength of the hydrogen bonding. In this investigation methanol was used as proton-donor for all the systems; attempts to use phenol (stronger acid) were unsuccessful since the bonded hydroxylic bands strongly interfered with the C-H stretching absorptions in the range 3000-3100 cm^{-1} and no reliable values could be obtained.

From table 2, where the $\Delta\nu_{OH}$ for the compounds investigated are reported, it appears that the values in quinoline-N-oxide and isoquinoline-N-oxide are almost the same and no change by hydrogen-deuterium substitution is observed. Being the magnitude of $\Delta\nu_{OH}$, when pyridine-N-oxide is used as pro-

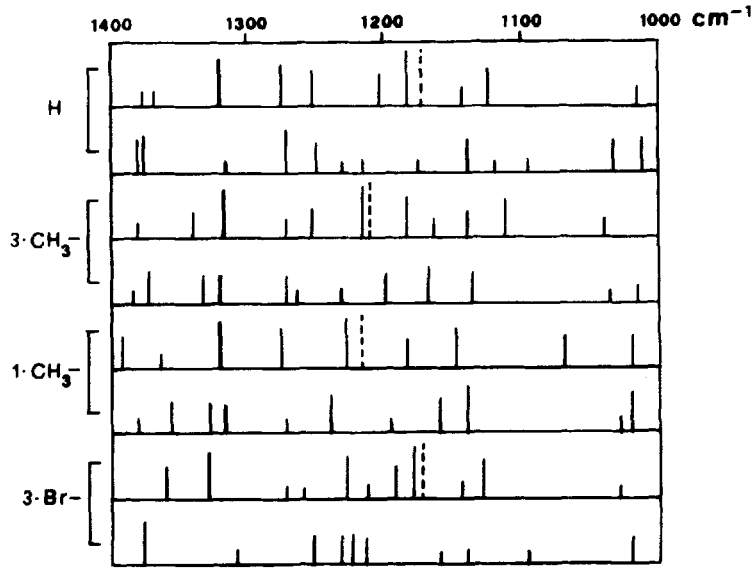

FIG. 2

Position and Relative Intensity of Absorption Bands of Substituted Isoquinolines and Isoquinoline-N-oxides in the Range 1400-1000 cm^{-1}. For each couple the spectrum of isoquinoline-N-oxide lies right above that of the corresponding isoquinoline. Dotted lines represent the shifts of the N→O band in the presence of CH_3OH; thicker lines represent the band at about 1300 cm^{-1} (see text).

ton-acceptor, very close to the previous values (6), it may be deduced that the resonance system involving the N→O group is rather similar in these series of compounds. In accordance to it, like in pyridine-N-oxides, a linear relationship $\Delta\nu/\sigma$ has been found for quinoline-N-oxides: for the former compounds the relation is $\Delta\nu_{OH}=285-120\sigma$ (for internal consistency of the data, the results were taken from (6)), while for the latter ones is $\Delta\nu_{OH}=276-170\sigma$. The higher slope of the straight line for quinoline-N-oxides suggests that the electronic effects of the substituents are slightly more effective in such compounds than in pyridine-N-oxides.

From the same table, it can be also seen that the capability of the α-substituents in reducing the hydrogen bonding is higher in quinoline-N--oxides than in isoquinoline-N-oxides.

TABLE 2

$\Delta\nu_{OH}$ Values (cm^{-1}) of Methanol when Quinoline-N-oxides and Isoquinoline-N--oxides are used as Proton-acceptors in C_2Cl_4 Solution

Quinoline-N-oxides				Isoquinoline-N-oxides	
Compound	$\Delta\nu_{OH}$	Compound	$\Delta\nu_{OH}$	Compound	$\Delta\nu_{OH}$
h-7	273	4•OCH_3-	324	h-7	274
d-7	273	4•Cl-	239	d-7	274
4•CH_3-	290	2•Cl-	186	3•CH_3-	274
3•CH_3-	287	3•Br-	210	1•CH_3-	287
2•CH_3-	247	2,6•CH_3-	253	4•Br-	244

In conclusion, there are two very strong absorptions which are characteristic of quinoline-N-oxides and isoquinoline-N-oxides; the one at higher frequencies (1300-1340 cm^{-1}) seems to be associated to a ring motion mainly involving the CN bond (in fact it is also present, although with a variable intensity, in the corresponding quinolines), while the band at lower frequencies (1180-1250 cm^{-1}), is considered mostly related to the N→O stretching mode. The existence of a high number of vibrational modes which absorb in the same region is probably the main reason for the mechanical interactions involving the NO vibration. Since such coupling is large enough to mask the electronic effects of the substituents, the magnitude of $\Delta\nu_{OH}$ seems to be a more valuable parameter to evaluate the electronic interactions between the NO group and the ring-substituents.

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