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138. **Hideyo Shindo :** Studies on the Infrared Spectra of Heterocyclic Compounds. IX.[1] Infrared Spectra of Monosubstituted Quinolines and their N-Oxides.

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In a previous work of this series, the infrared spectra of substituted pyridines[2,3] and their N-oxides,[4,5] and substituted pyrazines and their N-oxides[1] have been investigated, and the spectral characteristics of the compounds containing the aromatic ring-nitrogen and the N-oxide group were established and discussed. The purpose of the present study is to extend the studies on these monocyclic compounds to polynuclear compounds. Thus, the infrared spectra of substituted quinolines and their N-oxides were examined.

The infrared spectra of monomethylquinolines have been reported previously[6] and, more recently, those of polymethylquinolines were described by Karr, *et al.*[7] The infrared spectra of four kinds of 4-substituted quinolines and their N-oxides have been reported by Costa, *et al.*[8] but any detailed studies on the N-oxide compounds have not been made as yet.

In the present work, the infrared spectra of 20 monosubstituted quinolines, quinoline 1-oxide and its 19 derivatives were determined and the N-O stretching frequencies and the ring CH out-of-plane bending frequencies were assigned and discussed. The infrared spectra of quinoline 1-oxide and its monomethyl derivatives are shown in Fig. 1.

I. N-O Stretching Frequencies and Absorptions in the Region of 1000 and 1600 cm^{-1}

It has been well established[1,4,5] that the N-O stretching frequencies of substituted pyridine and pyrazine N-oxides appear as a strong absorption in the region of 1190 and 1350 cm^{-1}. In the resonance system of quinoline 1-oxide, just as in that of pyridine 1-oxide,[4,5] the contribution of mesomeric structure like (Ⅱ) is expected to be great, as well as that of the ionic structure like (Ⅲ). Consequently, the N-O bond in quinoline 1-oxide may be expected to have a considerable double-bond character, and many chemical[9] and physicochemical[10] studies indicate that the N-O bond in quinoline 1-oxide has

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[1] Part Ⅷ. H. Shindo : This Bulletin, 8, 33(1960).

[2] H. Shindo, N. Ikekawa : *Ibid.*, **4**, 192(1960).

[3] H. Shindo : *Ibid.*, **5**, 472(1957).

[4] *Idem* : *Ibid.*, **4**, 460(1956).

[5] *Idem* : *Ibid.*, **6**, 117(1958).

[6] H. Shindo, S. Tamura : *Ibid.*, **4**, 292(1956).

[7] C. Karr, Jr., P. A. Estep, A. J. Papa : J. Am. Chem. Soc., **81**, 152(1959).

[8] G. Costa, P. Blasina, G. Sartori : Univ. studi Trieste, Fac. Sci., Ist. chim., No. 9, 11(1955)(C. A., **50**, 11823(1956)).

[9] E. Ochiai : J. Org. Chem., **18**, 534(1953).

[10] H. Hirayama, T. Kubota : Yakugaku Zasshi, **72**, 1025(1952); T. Kubota : *Ibid.*, **74**, 831(1954), **75**, 1540, 1546(1955); *idem* : Nippon Kagaku Zasshi, **80**, 578(1959).

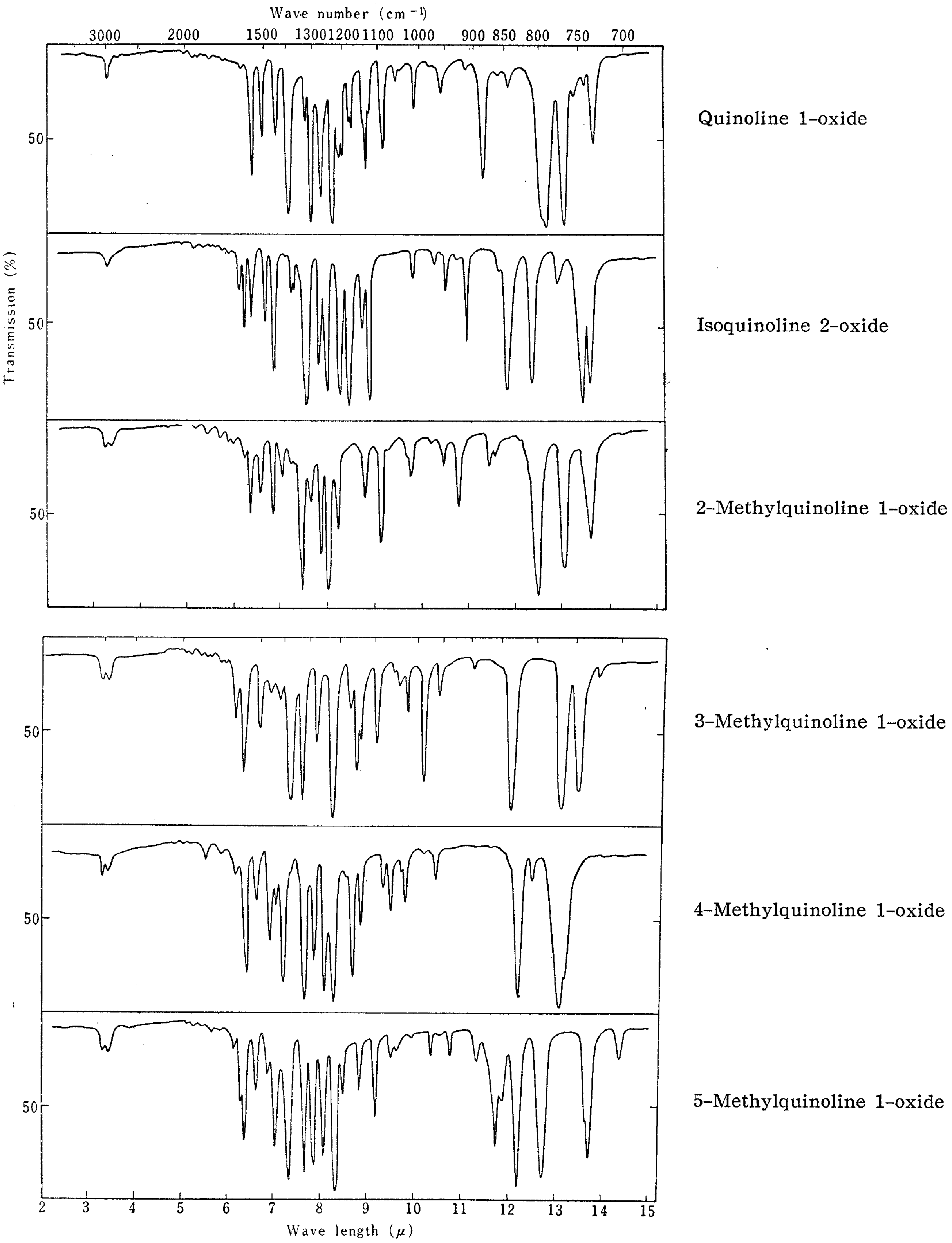


Fig. 1. Infrared Absorption Spectra of Quinoline 1-Oxide and its Monomethyl Derivatives (1)
(in CS_2 (4000~650 cm^{-1}) and in CCl_4 or $CHCl_3$ (1700~1400 cm^{-1}) solution)

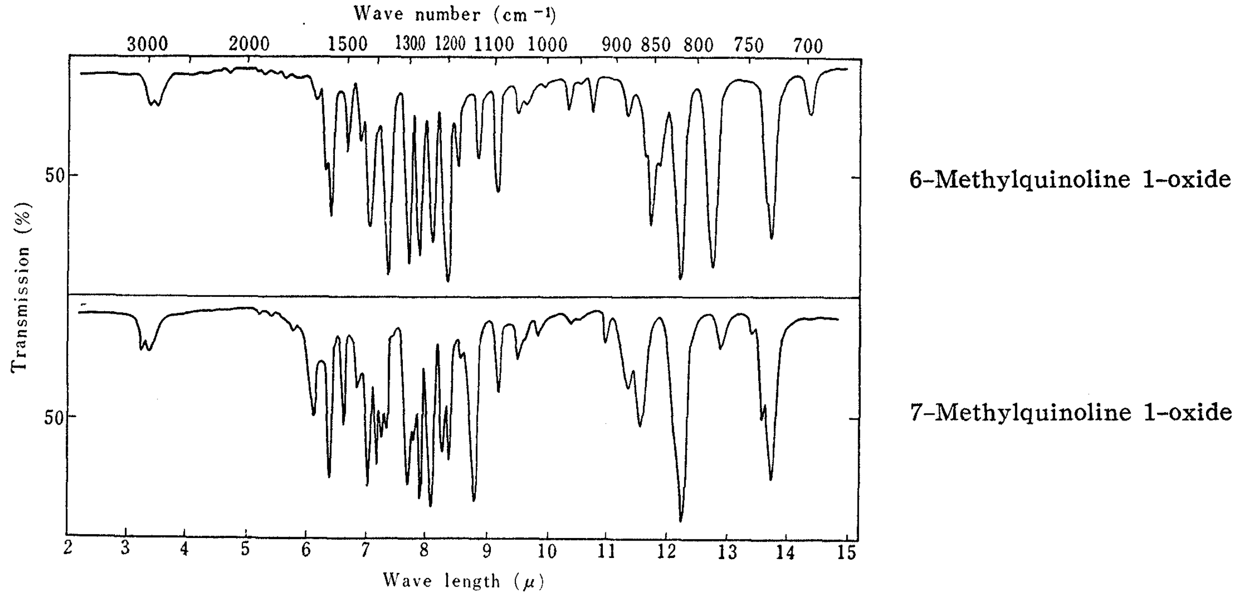
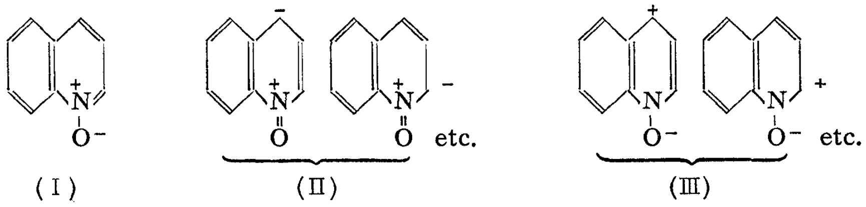


Fig. 1. Infrared Absorption Spectra of Quinoline 1-Oxide and its Monomethyl Derivatives (2)

essentially the same properties as that in pyridine 1-oxide. Therefore, the N-O stretching frequencies of quinoline 1-oxides can be expected to absorb strongly also in the region of 1190 and 1350 cm^{-1}.



In Table I, the prominent absorptions of quinoline 1-oxide and its monomethyl derivatives in the region of 1000 and 1650 cm^{-1} are compared with those of the corresponding quinolines. As can be seen from the Table, all N-oxide compounds showed three to five strong absorptions in the region of 1190 and 1350 cm^{-1}, while the corresponding quinolines did not show any absorption with a comparable strength but a series of weak absorptions originating mainly in the in-plane bending of ring hydrogen and the ring vibrations. In particular, two strong absorptions in the ranges of 1220~1260 cm^{-1} and 1300~1340 cm^{-1} are the most characteristic for the N-oxide compounds and are clearly attributed to the bands originating in the contribution of the N-O stretching vibration. However, exact positions of both of these two bands did not show any correlation to the structure. In polymethylpyridine 1-oxides,[4] it was seen that there exists a sensitive correlation between the N-O frequencies and the position of methyl groups, and that the introduction of a methyl group at α- or γ-position causes a regular shift of the N-O frequency to a lower frequency, in agreement with the expectation from the electron-donating nature of the methyl group. Contrary to the expectation, however, both 2- and 4-methylquinoline 1-oxides showed both of the above two bands at appreciably higher frequencies than those of quinoline 1-oxide.

On the other hand, it can be noted from Table I that there can be found a good correspondence between the absorption frequencies of the N-oxide compound and the parent quinoline, even for the band near 1240 cm^{-1}, and that the intensity of the bands which are attributable to the ring CH and the ring vibrations increases considerably in the

TABLE I. Prominent Absorptions of Quinoline and its Monomethyl Derivatives and their N-Oxides in the Region of 1000 and 1650 cm^{-1}

Observed maxima (cm^{-1})[a,b]

Compounds	1650~1400 cm^{-1}						1400~1300 cm^{-1} [c]		
Quinoline	1623 m	1599 m	1572 m	1506 m s	1435 w	1393 m	1373 m	1332 v w	1314 m
Quinoline 1-oxide	1623 v w		1570 m s	1515 m	1449 m	1395 s		1326 m	**1307 v s**
Isoquinoline	1630 m s	1592 m	1577 m	1504 m	1435 v w	1385 m	1377 m		
Isoquinoline 2-oxide	1639 w	1604 m	1574 m	1499 m	1456 m s	1381 w	1371 w	**1326 v s**	
2-Methylquinoline	1626 m	1605 m s	1560 w	1512 m s	1426 m	1374 w			1311 m
2-Methylquinoline 1-oxide		1603 v w	1565 m	1517 m	1455 m	1420 w		**1339 v s**	1309 m
3-Methylquinoline		1608 w	1571 w	1499 m s	1451 w	1415 v w	1373 w	1330 m	
3-Methylquinoline 1-oxide*	1637 m		1582 m s	1507 m	1451 w	1418 w	1368 s	**1327 s**	
4-Methylquinoline	1621 v w	1601 m s	1574 m	1513 m s	1458 m	1443 w	1393 m		1307 m
4-Methylquinoline 1-oxide*		1595 v w	1572 s	1516 m	1453 m s	1429 m	1395 s		**1311 v s**
5-Methylquinoline	1618 w	1600 m	1575 m	1506 m s	1474 w	1445 w	1399 m	1370 w	1319 m
5-Methylquinoline 1-oxide*	1613 w		1572 m s	1517 m	1452 m		1406 s	1362 v w	**1299 s**
6-Methylquinoline	1629 v w	1597 m	1570 m	1504 s		1445 m	1376 m	1323 w	
6-Methylquinoline 1-oxide		1587 m	1572 m s	1506 m	1456 w	1420 m s	1368 s		**1305 s**
7-Methylquinoline	1629 v w	1599 m	1572 w	1506 m s	1464 w	1456 w	1387 w	1359 w	1319 m
7-Methylquinoline 1-oxide	1630 m		1567 s	1515 m	1466 w	1420 s	1399 m s	1366 m	**1300 s**
8-Methylquinoline[d]	1618 v w	1597 w	1577 w	1502 m s	1473 w	1432 w	1392 m	1374 m	1314 m

Compounds	1300~1200 cm^{-1} [c]			1200~1000 cm^{-1}					
Quinoline		1230 v w	1214 w		1140 w	1119 m	1093 v w	1033 m	1014 w
Quinoline 1-oxide	1267 s	**1235 v s**	1205 m	1176 m	1136 m s	1129 m	1091 m	1056 w	1015 m
Isoquinoline	1272 m	1252 w	1215 w	1178 v w	1140 w			1036 m	1015 m
Isoquinoline 2-oxide	1277 m s	**1256 s**	1207 s	1183 s	1143 m	1126 s			1018 w
2-Methylquinoline		1248 v w	1220 m		1139 w	1116 m			1016 w
2-Methylquinoline 1-oxide	1272 m s	**1245 v s**	1214 m		1134 m	1093 m s			1022 w
3-Methylquinoline	1274 w	1232 v w	1205 w	1174 v w	1136 w	1124 w			1019 w
3-Methylquinoline 1-oxide*	1271 m	**1220 v s**		1166 w	1147 m s	1138 m	1094 m		1022 m
4-Methylquinoline		1244 m		1161 w	1138 m		1083 v w	1035 w	1021 w
4-Methylquinoline 1-oxide*	1277 m s	**1239 s**	1214 v s	1153 s	1131 m		1073 w	1057 m	1022 m
5-Methylquinoline		1242 v w	1198 w	1152 m		1076 w	1067 m	1035 v w	
5-Methylquinoline 1-oxide*	1264 s	**1240 s**	1202 m s	1189 m	1139 m		1070 m	1035 w	
6-Methylquinoline		1242 v w	1212 v w		1140 v w		1119 m	1034 w	
6-Methylquinoline 1-oxide	1274 s	**1243 s**	1203 v s	1181 m	1133 m		1092 m	1053 w	
7-Methylquinoline	1256 v w	1239 v w		1196 v w	1141 m		1118 m	1034 m	1007 v w
7-Methylquinoline 1-oxide	1267 s	**1238 v s**	1209 m s	1196 m s	1140 s		1089 m	1052 w	1016 v w
8-Methylquinoline[d]		1241 w	1207 v w	1165 w	1129 m	1076 m	1072 m	1037 v w	1029 w

a) v, very; s, strong; m, medium; w, weak.

b) In CCl_4 (1700~1400 cm^{-1}) and CS_2 (1400~1000 cm^{-1}) solution, * in $CHCl_3$ solution (1700~1400 cm^{-1}), cell thickness: 0.1 or 1.0 mm.

c) Characteristic N-O absorptions are in bold-face type.

d) Failed to be converted to the 1-oxide.

Table II. Prominent Absorptions of Substituted Quinoline 1-Oxides in the Region of 1000 and 1400 cm^{-1}

Substituent	Observed maxima (cm^{-1})$^{a),b)}$										
	1400~1200 cm^{-1} $^{c)}$						1200~1000 cm^{-1}				
3-CH_3	1368 s	**1327 s**		1271 m	**1220 v s**		1166 w	1147 m s	1094 m s		1025 m
-Br	1375 m s	1355 v s	**1308 s**	1264 m	**1218 v s**	1202 m	1161 w	1138 m s	1079 m		1019 w
-Br*	1354 v s		**1311 s**	1266 m	**1217 v s**		1165 w	1142 m s	1079 m		1020 w
-NO_2	1372 s	1348 s	**1318 m s**	1267 m	**1225 m s**	1196 m		1140 m	1080 m		1019 w
-NO_2*	1368 v s	1358 v s	**1322 s**	1268 w	**1225 s**	1211 m s	1164 w	1145 m	1099, 1085 m		1020 w
4-NH_2	1366 s		**1305 m**	1256 m	**1215 s**		1171 s	1140 v s	1072 m s	1031 m s	1016 m s
	1379 m s	1339 w	**1298 s**	1268, 1256 m s	**1220 v s**	1208 v s	1154 m	1131, 1115 m	1086 m	1033 m	1005 m
-$OCH_2C_2H_5$	1367 m s	1323 m	**1280 v s**	1235 m	1225 m	**1209 s**		1135 m	1092 s	1057 w	1019 m
-$OCH_2C_6H_5$*		1328 m s	**1289 v s**	1238 m	**1211 s**			1136 m	1092 s	1060 m	1021 m
-OCH_3	1391 m s	1323 m	**1279 v s**	1236 m s	1225 m s	**1209 s**	1157 w	1134 m	1098 v s	1060 m	1019 m
-OCH_3*	1402 s	1326 m s	**1287 s**		**1216 m s**	1193 m s	1170 m s	1146 w	1098 s	1056 m s	1022 w
-CH_3	1395 s		**1311 v s**	1277 m s	**1239 s**	1214 v s	1153 s	1131 m	1073 w	1057 m	1022 m
-H	1395 s	1326 m	**1307 v s**	1267 s	**1235 v s**	1205 m	1176 m	1136 m s	1091 m	1056 w	1015 m
-Cl	1376 s	1342 w	**1303 v s**	1256 m	**1225 s**	1205 w	1166 m	1142 m	1124 w	1063 m	1025 m
-Br	1372 s	1335 w	**1302 v s**	1253 m	**1227 s**	1202 w	1164 w	1139 m	1121 w	1062 m	1025 m
-Br*	1368 v s	1337 w	**1303 s**	1250 m s	**1230 m s**	1198 m	1166 m	1138 m	1122 w	1060 m	1025 w
-I	1366 s	1328 w	**1300 v s**	1250 m	**1227 s**	1199 w	1163 w	1135 m	1116 w	1063 m	1024 m
-CHO			**1318 v s**	1261 m	1248 m s	**1215 s**	1158 s	1134 m	1073 w	1052 s	
-CN	1393 m		**1314 v s**	1269 m	1242 m	**1224 m**	1155 m s	1134 m		1029 m	1007 w
-CN*	1395 m s	1364 m	**1306 v s**	1269 m	1244 m	**1224 m s**	1152 m s	1133 m		1028 m	1008 w
-NO_2	1391 m	1325 s	**1304 v s**		1248 m	1198 m	1166, 1156 m	1130 m	1068 w	1032 m	
-NO_2*	1387 m s	1343 s	**1300 v s**		1239 m	1195 m	1165, 1149 m s	1128 m s	1064 w	1028 m	

a) v, very; s, strong; m, medium; w, weak.

b) In dilute CS_2 solution, * Nujol mull or KBr pellet.

c) Characteristic N-O absorptions are in bold-face type.

N-oxide compounds. These facts seem to suggest the presence of a complex interaction between the N-O stretching vibration and the vibrations originating in quinoline ring, and the latter normally weak absorptions are considered to be enhanced in intensity due to coupling with the strong N-O stretching vibration.

The prominent absorptions of 3- and 4-substituted quinoline 1-oxides in the region of 1000 and 1400 cm^{-1} are shown in Table II. In accord with the result in methyl derivatives, all the N-oxide compounds exhibited two characteristic N-O absorptions in the ranges of $1280\sim1300\,cm^{-1}$ and $1215\sim1240\,cm^{-1}$, but the former band was more characteristic in its position and strong intensity. It was shown in substituted pyridine 1-oxide[4,5] that the N-O stretching frequencies showed a marked increase with increasing electron-attracting nature of the substituents, the frequencies forming a linear relationship to Hammett's substituent constant of the substituents. Therefore, the electronic effect of a substituent on quinoline ring, in particular that at 4-position, should also give a marked influence on the N-O stretching frequency, causing a shift in the same way as that in pyridine 1-oxides. However, none of the frequencies observed showed any correlation to the electronic nature of the substituent.

In Table II, the compounds are arranged in the sequence of increasing electron-attracting nature of a 4-substituent, and the frequency should increase in this sequence, but this was not the case. For example, 4-nitro- and 4-bromo derivatives showed the band near 1300 cm^{-1}, respectively 3 and 5 cm^{-1} lower in frequencies than that of quinoline 1-oxide, contrary to the expectation from the fact[5] that the N-O frequencies of 4-nitro- and 4-bromo-pyridine 1-oxides showed a respective shift of 38 and 6 cm^{-1} to a higher frequency than that of pyridine 1-oxide.

Such anomalous behavior of the N-O frequencies, as well as those observed in methyl derivatives, is considered to be due to the vibrational interaction between the N-O vibration and the ring hydrogen, and ring vibrations in the same region, and the resultant perturbation of the N-O frequency might show such anomalous behavior. The same explanation has been given for the anomalous behavior observed in β-methyl, acetyl, and ethoxycarbonyl derivatives of pyridine 1-oxide.[5]

It was previously shown[11] that the N-O stretching frequency of substituted pyridine 1-oxides showed a shift of $20\sim40\,cm^{-1}$ to a lower frequency following hydrogen-bond formation with methanol in non-polar solvent and that the compounds, whose N-O frequencies involve some vibrational interaction with other vibrations and show anomalous behaviors, could be differentiated by the fact that the magnitude of this shift was only $5\sim15\,cm^{-1}$.

The change in the spectra of quinoline 1-oxide in carbon tetrachloride solution on addition of methanol is shown in Fig. 2. The strong band at 1308 cm^{-1} which was the most characteristic for the N-oxide compounds did not show any appreciable shift, but that at 1235 cm^{-1} showed a slight shift to a lower frequency, the magnitude of the shift being only 8 cm^{-1}. This result indicates that none of the absorptions of quinoline 1-oxide in this region is sensitive to hydrogen-bond formation and, therefore, cannot be regarded as a pure N-O stretching mode, and that the N-O stretching mode appears as two or more separated absorptions as a result of coupling with other mode of vibrations.

The formation of hydrogen bond between quinoline 1-oxide and methanol was proved in the same way as that in pyridine 1-oxide.[11] When 0.02*M* of quinoline 1-oxide was dissolved in 0.01*M* dilute carbon tetrachloride solution of methanol, a new broad band due to hydrogen-bonded OH link appeared with its maximum at 3369 cm^{-1}. The observed $\Delta\nu$ value of 276 cm^{-1} is approximately equal to that of 285 cm^{-1} shown by pyridine 1-oxide[11] and this fact indicates that the hydrogen bonding ability, namely the ionic character, of

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[11] H. Shindo: This Bulletin, **7**, 791(1959).

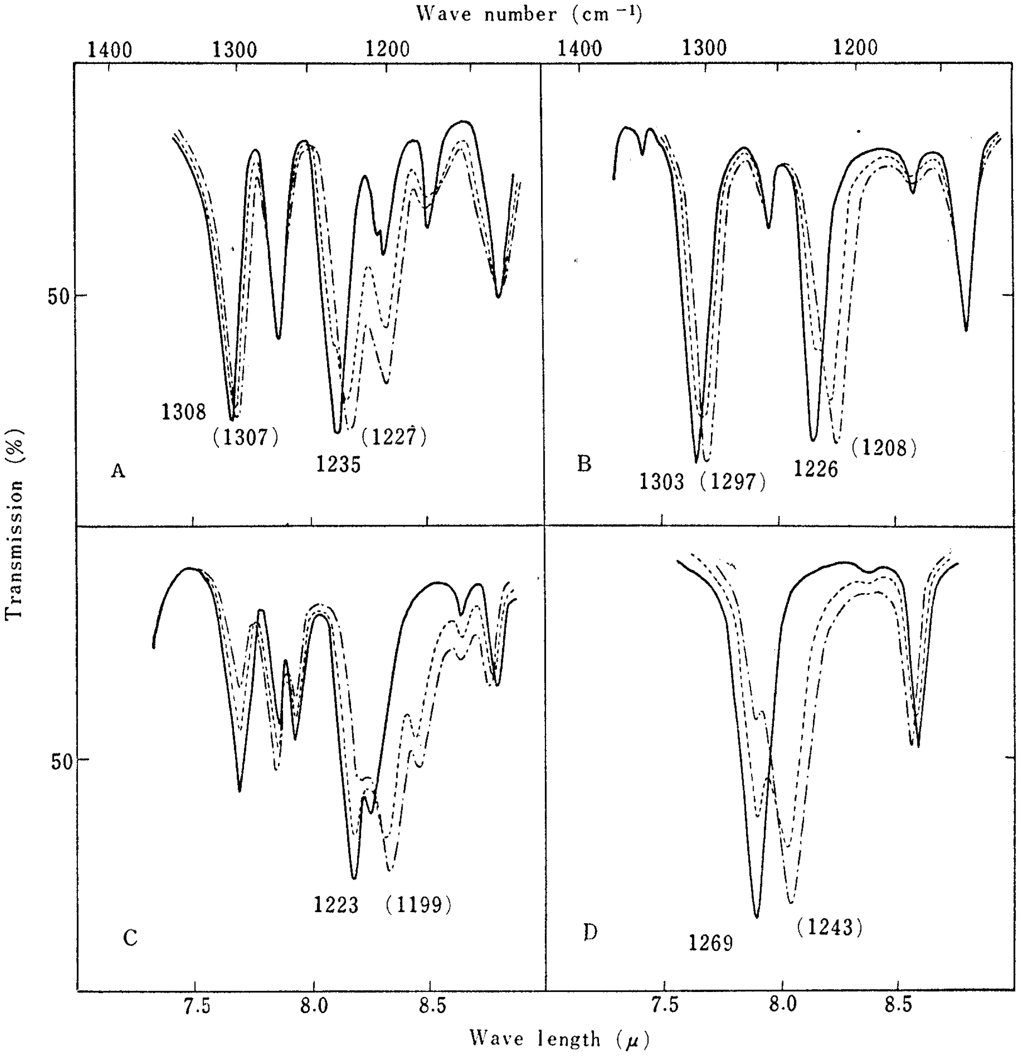


Fig. 2. Solvation Effect of Methanol on the N–O Frequency of Quinoline 1-Oxides

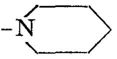
A : Quinoline 1-oxide B : 4-Bromoquinoline 1-oxide C : 4-Piperidinoquinoline 1-oxide
—— ca. 2% in CCl_4 ------ + ca. 5% MeOH –·–·– + ca. 10% MeOH
D : 4-Chloropyridine 1-oxide
—— 0.03M in CS_2 ------ +0.4M MeOH –·–·– +0.6M MeOH

the N–O bond is approximately equal in these two compounds.

In 4-bromo derivative, on the other hand, both strong bands at 1226 and 1303 cm^{-1} showed an appreciable shift to a lower frequency (Fig. 2), the magnitude of shift being 18 and 6 cm^{-1}, respectively. In this case, therefore, the N–O stretching mode can be considered to contribute mainly to these two absorptions. As shown in Table III, however, the behavior of absorptions on addition of methanol differs largely with individual compound. For example, the strong band at 1313 cm^{-1} in 4-cyano derivative showed a marked shift to a lower frequency, while the similar strong band at 1306 cm^{-1} in 4-nitro derivative did not show any appreciable shift. The only compound which showed a shift of over 20 cm^{-1} was 4-piperidino derivative and the strong band at 1223 cm^{-1} showed the shift of 24 cm^{-1} to a lower frequency. In this case, the N–O stretching mode is considered to contribute mainly to this single absorption (Fig. 2).

For the N–O frequency of isoquinoline 2-oxide, the value of 1274 cm^{-1} was predicted on the basis of the linear relationship[5] between the N–O frequency of substituted pyridine 1-oxides and Hammett's σ-value of the substituents, $\nu=1263.5+58.6\sigma$, applying 0.17 as

Table III. Solvation Effect on the Absorptions of Substituted Quinoline 1-Oxides in the Region of 1100 and 1400 cm^{-1}

Substituent	Observed maxima (cm^{-1})				
	in CCl_4	CCl_4+10% MeOH	$\Delta\nu$	in H_2O	$\Delta\nu$
4-NO_2	1343 m	1343 m			
	1306 v s	1302 v s	−4		
	1248 w	1239 m	−9		
4-NO_2, 6-CH_3	1354 s	1352 s			
	1272 s	1256 s	−16		
	1198 m	1196 s			
4-CN	1313 v s	1304 v s	−10		
	1241 m	1237 m	−4		
	1223 m	1218 m	−5		
4-Br	1373 s	1371 s			
	1303 s	1297 s	−6		
	1226 s	1208 s	−18		
4-Cl	1378 s	1378 s		1378	
	1304 s	1300 s	−4	1299	−5
	1224 s	1209 s	−15	1206	−18
H	1397 s	1395 s		1397	
	1308 s	1307 s		1309	
	1267 m s	1266 m s		1266	
	1235 s	1227 s	−8	1225	−10
	1205 w	1205 m s *		1205	
Iso-, H	1328 s	1326 s		1330	
	1277 s	1273 m	−4	1273	−4
	1255 m s	1253 m s		1253	
	1206 m s	1206 m s		1206	
	1183 s	1171 s	−12	1167	−16
4-CH_3	1395 s	1393 s			
	1310 v s	1310 v s			
	1277 m	1275 m			
	1239 s	1239 s			
	1212 s	1206 s	−6		
	1156 s	1157 s			
4-	1300 s	1200 s			
	1269 m s	1271 m s		1269	
	1258 m s	1258 m s		1256	
	1223 v s	1199 v s	−24	1197	−26
	1209 s	1181 sh	−28	1177	−32

* Marked increase in intensity may be due to the contribution of the bonded N-O absorption (see Reference 11).

the σ-value for 3,4-$(CH)_4$ group.[12] However, the strongest band appeared at 1328 cm^{-1} and only a band of medium strength appeared at 1277 cm^{-1}, near the predicted position, and furthermore the largest shift by methanol was observed for the band at the considerably low frequency of 1183 cm^{-1}.

From the foregoing results, it may be concluded that, in substituted quinoline 1-oxides, the N-O stretching vibration usually does not exhibit a single absorption band, but its contribution separates into two or more absorptions in the region of 1150 and 1350 cm^{-1} due to coupling with the vibrations originating in quinoline ring, and that the band which may involve the largest contribution of the N-O stretching mode can be selected by examining the solvation effect, but their frequencies do not show any correlation to the structure.

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[12] H. H. Jaffé : Chem. Revs., **53**, 191(1953).

The occurrence of such a complex coupling in quinoline 1-oxide and its derivatives, which is assumed to be characteristic to polynuclear heteroaromatic N-oxides, in contrast to its absence in pyridine 1-oxide and most of its derivatives, is considered to be due to the following two reasons; i) marked decrease in molecular symmetry from C_{2V} to C_S on passing from pyridine 1-oxide to quinoline 1-oxide, which results in a marked increase of the possibility of such coupling, and ii) increase in the number of absorption bands originating in the ring and ring-hydrogen vibrations which are available for such coupling, on passing from pyridine to quinoline ring.

At any rate, the appearance of strong absorptions in the region of 1190 and 1350 cm^{-1}, in particular those in the ranges of 1280~1340 cm^{-1} and 1210~1260 cm^{-1}, is very characteristic to quinoline 1-oxide derivatives.

II. Ring CH Out-of-plane Bending Frequencies

The strong absorptions observed in the region of 700 and 900 cm^{-1} are assigned to the out-of-plane bending frequencies of aromatic ring hydrogen. As shown in Table IV, these frequencies of monosubstituted quinolines were easily correlated to their structures by considering the number of adjacent free hydrogen atoms on the componental carbocyclic and heterocyclic rings, in the same way as that in methylquinolines.[6,7] Thus, 2-, 3-, and 4-monosubstituted derivatives always showed a strong absorption in the region of 740 and 760 cm^{-1}, corresponding to four adjacent hydrogen atoms on unsubstituted carbocyclic ring, and a strong absorption in the ranges of 814~843, 885~924, and 827~858 cm^{-1}, respectively, corresponding to two, one, and two adjacent hydrogen atoms on heterocyclic ring. Furthermore, 2- and 4-monosubstituted derivatives can be differentiated by the fact that in the former the band near 820 cm^{-1} is always stronger than that near 750 cm^{-1}, while in the latter this relative intensity is always reversed.

The corresponding absorptions of monosubstituted quinoline 1-oxides can also be interpreted in the same way as that in the corresponding quinolines, and, for example, 4-substituted derivatives always showed a very strong absorption in the region of 760 and 770 cm^{-1} and a strong absorption in the region of 805 and 830 cm^{-1}. Furthermore, as was found in substituted pyridine[5] and pyrazine N-oxides,[1] a distinct regularity was found in the direction of shift of these frequencies when they are compared to those of the corresponding substituted quinolines. As can be seen from Table IV, 4-monosubstituted quinoline 1-oxides showed a band near 820 cm^{-1} always at a lower frequency than that of the corresponding quinolines, while that near 770 cm^{-1}, always at a slightly higher frequency, regardless of the nature of the substituent. On the other hand, quinoline 1-oxide and its 2-, 3-, 5-, 6-, and 7-methyl derivatives showed all these absorptions at an appreciably lower frequency than those of the corresponding quinolines, and the direction of these shifts is considered to be also constant regardless of the nature of the substituent, depending only upon the type of substitution. It was shown in the previous paper[1] that the direction of the shift of frequencies in pyrazine and pyrimidine N-oxides from those of the corresponding bases agreed with the correlation found in the corresponding substitution types of pyridine 1-oxides. The same relationship was also found in the frequencies originating in heterocyclic ring of quinoline 1-oxides, and the above result that the frequencies of quinoline 1-oxide and its 5-, 6-, and 7-substituted, 2-substituted, and 4-substituted derivatives showed a shift to lower frequency is in agreement with the fact[4] that the frequency of the corresponding substitution types of pyridine 1-oxide, that is, 2,3-dimethyl-, and 2,3,6- and 2,3,4-trimethyl-pyridine 1-oxides, showed shift to a lower frequency than those of the corresponding pyridines.

Table IV. Ring CH Out-of-plane Bending Frequencies of Substituted Quinolines and their N-Oxides (cm^{-1})

Substituent	Quinolines				Quinoline N-oxides			
	δ_{CH} (out-of-plane)		Other prominent bands		δ_{CH} (out-of-plane) ($\varDelta\nu$)[a]		Other prominent bands	
H	803 v s	734 m s		786 s	789 v s (−14)	725 m (− 9)	885 m s	766 v s
Iso-	825 v s	739 v s	859 m		809 s (−16)	745 v s (+ 6)	844 s	736 s
2-CH_3	816 v s	743 s		782 m s	801 v s (−15)	735 s (− 8)		766 s
-Cl	816 v s	748 s	854 m s	778 m s				
-Br	814 v s	745 s	836 m	776 m s				
-CHO	829 v s	747 v s	885 m	786 m	b)			
-CN	827 v s	753 s		784 m				
3-CH_3	885 m s	749 v s	859 m	784 m s	833 s (−52)	744 s (− 5)		765 s
-NH_2*	887 m s	745 v s	838 m	780 m s	b)			
-Br	892 m s	747 v s	847 m	778 m s	831 v s (−61)	741 m s (− 6)	839 sh	764 s
-CN	913 m s	751 v s	862 m	783 m s	b)			
-NO_2	924 m	758 v s	805 s	782 s	880 m (−44)	755 s (− 3)	792 s	765 s
-NO_2*	929 m s	767 s	806 s	790 s	903 m (−26)	758 m s (− 9)	797 v s	779 v s
4-CH_3	838 s	756 v s	860 m		820 s (−18)	763 v s (+14)		
-N 	827 s	766 v s			816 s (−11)	768 v s (+ 2)	794 m s	738 s
-$OCH_2C_6H_5$	812 s	764 v s		734 m s	805 s (− 7)	768 s (+ 4)		758 m s
-$OCH_2C_6H_5$*	822 s	769 v s	879 m s	761 v s	807 m s (−15)	777 v s (+ 8)	843 m s	738 s
-OCH_3	b)				806 s	766, 756 v s		
-Cl	833 s	759 v s	822 m s	812 m	817 s (−16)	764 v s (+ 5)	796 m	740 m s
-Br	831 s	758 v s	802 m s		816 s (−15)	764 v s (+ 6)	795 m	734 m
-I	831 s	756 v s	792 m		816 s (−15)	762 v s (+ 6)	794 m	731 m
-CHO	840 s	760 v s			821 m s (−19)	772 s (+12)		
-CN	b)				825 m s	767 s		
-NO_2	837 m	766 m s	883 m	787 m	829 s (− 8)	766 v s (± 0)	791 m	740 m
-NO_2*	858 m s	766 v s	872 s	787 m s	842 s (−16)	765 v s (− 1)	788 m	738 m s
-NH_2*	829 m s	758 s	885 m s		824 s (− 5)	770 v s (+12)	863 m	756 v s
5-CH_3	801 v s		816 m s		783 v s (−18)		789 sh	718 m
6-CH_3	875 m, 828 v s, 795 m s			761 m	854 m s (−21), 820 v s (−10), 786 s (− 9)			729 s
7-CH_4	884 m, 828 v s, 782 m s				864 m s (−20), 819 v s (− 9), 729 s (−53)			

* In Nujol mull, others in CS_2 solution.

a) Frequency differences as compared to those of the parent quinolines in the same state.

b) Not measured.

Experimental

Material—Quinoline 1-oxide, isoquinoline 2-oxide, and six monomethylquinoline 1-oxides were prepared from the corresponding quinolines by oxidation with H_2O_2 according to the method of Ochiai.[9] Samples were purified by distillation under a reduced pressure and the purity was checked by melting point and elemental analyses of their picrates. The quinoline bases used as the starting material were pure samples prepared and used in the previous work.[6] Oxidation of 8-methylquinoline by the usual way did not give the 1-oxide, but gave a product with a high melting point of 216° (white needles from benzene-ligroine, insoluble in CCl_4 and CS_2. *Anal.* Found: C, 75.59; H, 5.61; N, 8.65). Other 12 monosubstituted quinoline 1-oxides were supplied by the Faculty of Pharmaceutical Sciences, University of Tokyo. Twenty monosubstituted quinolines used were those prepared in the Faculty of Pharmaceutical Sciences, University of Tokyo, and in this Laboratory.

Method—Infrared spectra were measured with a Perkin-Elmer Model 21 double-beam spectrophotometer provided with a NaCl prism. Quinoline 1-oxide and its methyl derivatives were measured as 0.5~0.6% solution in CS_2 with the cell of 1.0 mm. thickness and the region of 1400~1700 cm^{-1} as 5.0~6.0% solution in CCl_4 or $CHCl_3$ with the cell of 0.1 mm. thickness. Solution spectra of other substituted quinoline 1-oxides and substituted qunolines were measured as 0.5% or saturated solution in CS_2 with the cell of 1.0~5.0 mm. thickness depending upon the solubility of the sample. Solid spectra were measured as Nujol mull or KBr pellet. Experimental method on the solvation effect of MeOH and water (Fig. 2, Table III) was the same as that reported in the previous paper.[11]

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Summary

Infrared spectra of 20 kinds of monosubstituted quinolines, quinoline 1-oxides, and isoquinoline 2-oxides, and 18 kinds of monosubstituted quinoline 1-oxides were determined.

By comparison with the spectra of corresponding quinolines, two strong absorptions in the regions of 1280~1340 cm^{-1} and 1210~1260 cm^{-1} of the N-oxide compounds were assigned to the characteristic N-O absorptions. By examining the solvation effect of methanol and water, however, it was clarified that the N-O stretching vibration contributes to two or more absorptions in the region of 1150 and 1350 cm^{-1} due to complex coupling with the vibrations originating in the quinoline ring and ring hydrogens, and there was not found any correlation between these frequencies and the structure.

Ring CH out-of-plane bending frequencies were assigned and interpreted by considering the number of adjacent free hydrogens on heterocyclic and carbocyclic rings, and it was found that all the frequencies of monosubstituted quinoline 1-oxides, except the band near 770 cm^{-1} in 4-substituted derivatives, show an appreciable shift to a lower frequency than those of the corresponding quinolines.

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