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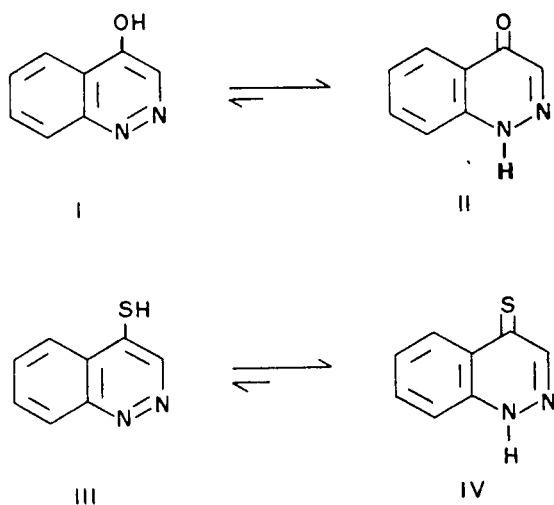
Cinnoline Chemistry X. The Infrared Spectra of Halogen Substituted 4-Hydroxy- and 4-Mercaptocinnolines

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The infrared spectra of a series of 4-hydroxy- and 4-mercaptocinnolines substituted with fluorine, chlorine or bromine in the 5-, 6-, 7- and 8-position have been obtained in potassium bromide discs between 4000 and 400 cm^{-1} . Assignments for most of these bands have been made.

A few reports on the infrared spectra of bicyclic heteroaromatic compounds have been published, primarily quinolines. Recently these have been reviewed by Katritzky (1). Little information is available for the cinnolines; a series of spectra has been reported (2,3), but few assignments have been attempted.

In this paper are reported the spectra of a series of 4-hydroxy- and 4-mercaptocinnolines monosubstituted with fluorine, chlorine or bromine in the benzenoid part of the cinnoline system. The 4-hydroxycinnolines (I) and the 4-mercaptocinnolines (III) exist as the tautomers 1,4-dihydro-4-cinnolones (II) and 1,4-dihydro-4-cinnolinethiones (IV), respectively, both in solution and in the solid state. These structures give rise to NH and C=O bands rather than hydroxyl bands.



EXPERIMENTAL

The spectra were recorded on a Perkin-Elmer 337 spectrophotometer between 4000 and 400 cm^{-1} using the potassium bromide disc technique. Intensity measurements are not precise and therefore are recorded as strong, medium or weak (4).

The preparation of the cinnolines was reported in a previous paper in this series (5). Samples were purified by recrystallizations to meet analytical

standards. A single compound, 5-bromo-4-mercaptocinnoline, was not reported in (5). It was prepared from 5-bromo-4-hydroxycinnoline by refluxing for a few minutes with phosphorus pentasulfide in dry pyridine according to the procedure described in (5).

Anal. Calcd. for $\text{C}_8\text{H}_5\text{BrN}_2\text{S}$: C, 39.85; H, 2.09; N, 11.61; S, 13.29. Found: C, 39.93; H, 2.15; N, 11.98; S, 13.11.

RESULTS AND DISCUSSION

With a few exceptions all bands between 4000 and 400 cm^{-1} could be assigned to vibrations of the ring skeleton, the substituents or the hydrogen atoms on the cinnoline ring.

The 3500 - 2500 cm^{-1} Region.

The 3500 - 2500 cm^{-1} region is dominated by a broad NH stretching band of high intensity from *ca.* 3250 to *ca.* 2500 cm^{-1} in the spectra of both 4-hydroxy- and 4-mercaptocinnolines in the solid state. The broadness of the band is due to intermolecular hydrogen bonding, $\text{N-H}\cdots\text{O}$ or $\text{N-H}\cdots\text{S}$, as observed for many similar molecules (1). A dilute solution of 4-mercaptocinnoline in chloroform shows the free ν NH band at 3400 cm^{-1} .

The broad ν NH band of the 4-hydroxy- and 4-mercaptocinnolines in the solid state generally appears divided into three sections, each with several maxima. One at 3250 - 3150 cm^{-1} , a second with one to three peaks between 3100 and 3000 cm^{-1} and a third with a rather constant maximum at 2950 cm^{-1} . The first and the third of these sections arise from the $\text{N-H}\cdots\text{O}$ or $\text{N-H}\cdots\text{S}$ intermolecular hydrogen bonding. Possibly the individual peaks at 3100 - 3000 cm^{-1} should be assigned to the CH stretching vibrations.

The 1600 - 1350 cm^{-1} Region.

The bands arising from the ring stretching vibrations in this region are listed in table I. For bicyclic aromatic systems of the naphthalene type nine normal modes of C-C and C-N character are expected, of which eight occur in this region. The ninth mode for naphthalene has been assigned to a

TABLE I

Ring Stretching Bands in the 1600 - 1350 cm^{-1} Region (a)

Cinnoline								
4-mercapto	1610 m	1577 w	1557 s	1480 s	1455 s	1412 s	1383 m	1335 w
5-chloro-4-mercapto	1605 s	1580 w	1550 s	1470 s	1453 s	1390 s	1380 m	1345 m
5-bromo-4-mercapto	1595 s	1570 w	1543 s	1470 m	1443 s	-	1382 m	1335 w
6-fluoro-4-mercapto	1627 w	1588 s	1565 s	1488 s	(1467) 1455 s	1420 s	1387 m	1370 m
6-chloro-4-mercapto	1610 w	(1575)	1563 s	1497 w	1460 s	1403 s	1377 m	1360 m
6-bromo-4-mercapto	1603 w	(1575)	1565 s (1555)	(1480)	(1465) 1453 s	1397 m	1373 w	1352 m
7-fluoro-4-mercapto	1625 s	1585 m	1555 s	(1495) 1485 s	1445 m	1423 s 1407 m	1383 w	1368 m
7-chloro-4-mercapto	1607 s	1583 w	1560 s	1480 m (1468)	1435 s	1420 s	-	1368 s
8-fluoro-4-mercapto	1623 w	1582 s	1545 s	1480 m	1457 s (1435)	1420 s	1380 s	1352 w
8-chloro-4-mercapto	1604 m	-	1558 s	1480 m	-	1422 s	1365 m	1340 w
8-bromo-4-mercapto	1600 s	(1562)	1550 s	1477 s	-	1420 s	1368 s	1338 m
4-hydroxy	(1604)	(1593)	(1560)	1487 m	1470 s	1433 m	1380 s	1342 w
5-chloro-4-hydroxy	(1606)	1593 s	(1560)	1490 w 1480 m	1463 s	1407 m	1385 s	1335 m
5-bromo-4-hydroxy	1597 s	1588 s	(1556)	1485 w 1471 w	1450 s	1400 w	1375 s	1350 w 1330 w
6-fluoro-4-hydroxy	(1605) (1618)	(-)	1555 s	1487 s	-	1418 m	1388 s	1360 w
6-chloro-4-hydroxy	(1605)	(-)	(1562)	1478 s	1470 s	1423 w 1413 w	1370 s	1352 m
6-bromo-4-hydroxy	(1607)	(-)	1548 s	(1475) 1508 w	1465 s (1472)	1417 w	1367 s	1347 w
7-fluoro-4-hydroxy	(-)	(-)	1560 s	1500 w	1460 s	1399 w	1370 s	1348 w
7-chloro-4-hydroxy	(-)	(-)	1553 s	1492 m	1443 s	1415 s	1370 s	(1345)
7-bromo-4-hydroxy	(-)	(-)	1547 s	1480 m	1437 s	1418 w	1372 w	1356 s
8-fluoro-4-hydroxy	(-)	(-)	1552 s	1495 m	1460 w	1437 m	(1377) 1370 s	1340 w
8-chloro-4-hydroxy	(-)	(-)	1563 s	1492 s	1437 w	1427 s	1370 s	1348 s
8-bromo-4-hydroxy	(-)	1568 w	1553 s	1489 s	1434 m	1413 m	1367 w 1353 w	1338 s
Arithmetical means and standard deviation:								
4-hydroxycinnolines	-	-	1556 \pm 5	1487 \pm 9	1454 \pm 14	1417 \pm 11	1373 \pm 7	1345 \pm 8
4-mercaptocinnolines	1610 \pm 10	1578 \pm 7	1555 \pm 7	1481 \pm 8	1451 \pm 8	1412 \pm 11	1377 \pm 6	1351 \pm 12
All cinnolines			1555 \pm 6	1484 \pm 9	1453 \pm 12	1415 \pm 11	1375 \pm 7	1348 \pm 12

(a) Key to abbreviations and symbols: - signifies band is missing; (-) signifies band is masked by stronger absorption; (1560) signifies band at 1560 cm^{-1} appears as a shoulder and intensity is not given; s = strong; m = medium; w = weak.

TABLE II

The 1350 - 1000 cm^{-1} Region (a)

Cinnoline	Ring ?			β CH			Ring ?		
4-hydroxy	1308 s	1250 s	-	1139 m	1123 m	1096 m 1082 s	1048 w	1013 w 1028 m	
4-mercapto	(1328)	1263 s	-	1150 s	1123 m	1108 s 1099 s	1038 w	1020 m (1015)	
5-chloro-4-hydroxy	1289 m	-	1197 m	-		1108 s	1061 w	-	
5-bromo-4-hydroxy	1288 m	-	1196 m	1142 w		1105 s	1067 w	-	
5-chloro-4-mercapto	1308 m	1243 s	1216 s	1142 m		(1119) 1111 s	(-)	1013 w	
5-bromo-4-mercapto	1307 m	1242 s	1210 s	1142 m		(1118) 1110 s	(-)	1014 w	
8-fluoro-4-hydroxy	1310 w (1298)	1260 s	1250 s	1150 m 1145 m		1109 s	1067 w 1052 m	-	
8-chloro-4-hydroxy	1297 w	1249 w	1230 w	1160 m		1097 s	(1048)	-	
8-bromo-4-hydroxy	1292 w	1247 w	-	1140 w		1082 s	(-)	-	
8-fluoro-4-mercapto	1331 s (1318)	1258 s	1242 s	(1151) 1135 m		1090 s	1060 m 1040 s	(1020)	
8-chloro-4-mercapto	1320 s	1250 s	1227 s	1148 m		1097 s	1062 m	-	
8-bromo-4-mercapto	1324 s	1250 w	1220 s	1149 w		1091 s	1058 w	-	
6-fluoro-4-hydroxy	1291 s	1250 m	1232 m	-	1134 s	1114 m	1061 m 1058 m	-	
6-chloro-4-hydroxy	1296 m	1241 w	-	1145 m 1140 m	1132 m 1128 m	(1100)	1063 m 1059 m	-	
6-bromo-4-hydroxy	1286 s	1246 m (1239)	-	1144 m	1121 m	1094 m	1059 m	-	
6-fluoro-4-mercapto	1319 m	(1255) 1248 s	-	1150 s	1132 s	1113 s (1109)	1063 w	1012 s	
6-chloro-4-mercapto	1314 s	1257 s	1230 w	(1153)	1144 m	1094 s	1048 w (1040)	1020 s	
6-bromo-4-mercapto	1314 m	1257 s	1228 w	1149 m	1138 m	1094 s	1045 w	1021 s	
7-fluoro-4-hydroxy	1293 s	1267 s	1236 w	(-)	1131 m	1100 s 1082 s	1038 w	-	
7-chloro-4-hydroxy	1291 s	1239 m	1224 m	1146 w	1119 w	1108 w 1092 w	(-)	1014 w	
7-bromo-4-hydroxy	1289 s	1246 s	1224 m	1145 m	1120 w	1102 w 1091 w	(-)	1012 w	
7-fluoro-4-mercapto	1328 s	1259 s	1239 s	(-)	1131 m 1111 w	1100 s	1038 w	1021 s (1011)	
7-chloro-4-mercapto	1328 s	1251 m	1227 m	1151 m	(1138)	1107 s	(-)	1018 m (1010)	

Mean values and standard deviations:

4-hydroxycinnolines	1293 \pm 6	1249 \pm 7	1224 \pm 17	1145 \pm 6		1099 \pm 9	1055 \pm 9	
4-mercaptocinnolines	1320 \pm 7	1253 \pm 6	1227 \pm 10	1148 \pm 4		1101 \pm 9	1048 \pm 9	
5- and 8-substituted		1250 \pm 6	(1221 \pm 17)	1146 \pm 6		1101 \pm 11	1058 \pm 6	
6- and 7-substituted		1251 \pm 8	1230 \pm 5	1148 \pm 3	1130 \pm 8	1100 \pm 7	1051 \pm 10	
All cinnolines	1306 \pm 14	1251 \pm 7	1225 \pm 14	1147 \pm 5		1100 \pm 9	1053 \pm 10	1015 \pm 9

(a) Key to abbreviations and symbols: - signifies band is missing; (-) signifies band is masked by stronger absorption; (1560) signifies band at 1560 cm^{-1} appears as a shoulder and intensity is not given; s = strong; m = medium; w = weak.

TABLE III

Bands in the 1200 - 1050 cm^{-1} Region Involving Substituents

	$\nu\text{C=S}$ or νCO	F	Cl	Br
4-mercaptocinnolines:				
Unsubstituted	1183 s			
5-chloro	1171 s		1071 s	
5-bromo	1170 s			1061 s
6-fluoro	-	1211 s		
6-chloro	1175 s		1072 s	
6-bromo	1174 s			1061 s
7-fluoro	1158 s	1198 m 1184 s		
7-chloro	1187 s		1075 s	
8-fluoro	1164 s	1177 s		
8-chloro	1164 s		1050 s	
8-bromo	1162 s			1047 s (1033)
	1171 \pm 9			
4-hydroxycinnoline				
unsubstituted	1570			
5-chloro	1568		1044 s	
5-bromo	1565			1041 s
6-fluoro	1580	1205 s 1192 s		
6-chloro	1580		1086 s	
6-bromo	1575			1080 s
7-fluoro	1600	1172 s		
7-chloro	1600		1067 s	
7-bromo	1580 1565			1053 s
8-fluoro	1600	1165 s		
8-chloro	1572		1061 s	
8-bromo	1628 1600			1050 s
	1584 \pm 17			

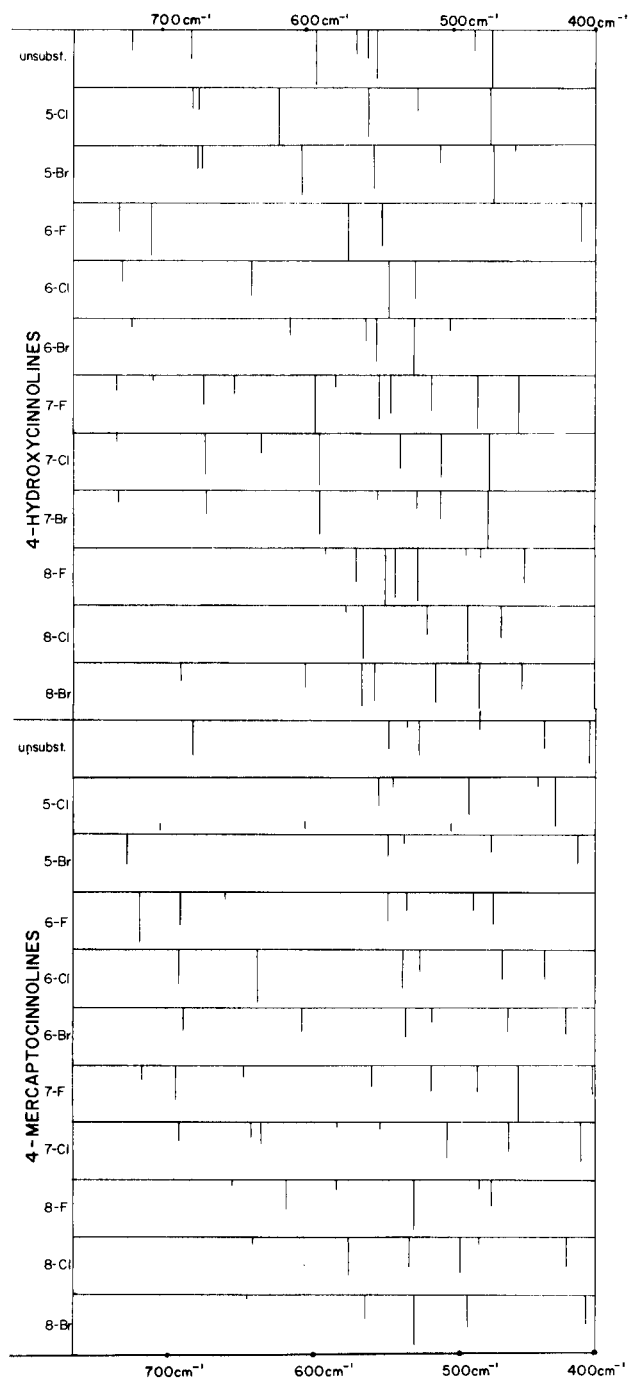


FIGURE 1

TABLE IV

The 1000 - 750 cm^{-1} Region (a)

Cinnoline	CH	Skeleton ?	CH (3-H)	CH	CH	CH	NH ?
4-hydroxy	967 w	-	900 s 879 m		800 s 782 m	765 s	845 s
4-mercapto	969 w	911 m	889 w 870 w		809 s	750 s	770 s
5-chloro-4-hydroxy	971 m	925 w	881 m		(804)	798 s	825 s
5-bromo-4-hydroxy	950 m	-	882 m		(802)	795 s	(807)
5-chloro-4-mercapto	970 w	938 s	894 m (884)		800 m	790 s	(755)
5-bromo-4-mercapto	977 w	911 m	904 m		801 s	(790)	766 m
8-fluoro-4-hydroxy	983 w 971 w	930 m	888 m 872 s		830 830 m	791 m	-
8-chloro-4-hydroxy	-	926 w	905 w 889 s		820 s 814 s	788 s	-
8-bromo-4-hydroxy	-	912 s	906 m		802 s	779 m	-
8-fluoro-4-mercapto	978 w	-	897 s		809 s	790 m	768 w
8-chloro-4-mercapto	971 m	924 m	896 s 876 m		817 m	799 s	(760)
8-bromo-4-mercapto	-	918 w	906 m 877 m		810 m	795 s	-
6-fluoro-4-hydroxy	-	928 s	895 m 887 m	879 m	823 (819)	766 m	(-)
6-chloro-4-hydroxy	951 w 945 w	(913) 907 s	891 s (887)	857 w 853 w	819 s	768 m	(-)
6-bromo-4-hydroxy	-	905 s	880 m	-	837 s 820 s	763 m	(-)
6-fluoro-4-mercapto	-	943 w	889 m (884)	867 w	812 s	(-)	787 m
6-chloro-4-mercapto	-	921 w 917 w	891 m 882 m	858 m	811 s	(-)	772 m
6-bromo-4-mercapto	-	920 w	902 m 882 m	844 w	817 s 831 m	(-)	770 m
7-fluoro-4-hydroxy	-	958 m	(891) 879 s	864 s 858 s	821 m 801 m	759 s	(-)
7-chloro-4-hydroxy	-	925 m	888 s	858 m 844 s	831 s	763 m	800 m
7-bromo-4-hydroxy	-	911 m	872 s	(850)	838 s	759 w	(795)
7-fluoro-4-mercapto	-	943 s	896 s	-	844 s 832 m	763 m	(-)
7-chloro-4-mercapto	-	913 m	892 m	-	846 s 841 s 819 s	(-)	775 m

Mean values and standard deviations:

4-hydroxycinnolines		923 \pm 14	886 \pm 8		817 \pm 14	775 \pm 14	(814)
4-mercaptocinnolines		924 \pm 12	891 \pm 6		814 \pm 13	782 \pm 17	(769)
5- and 8-substituted	970 \pm 8	923 \pm 9	891 \pm 8		810 \pm 10	792 \pm 6	
6- and 8-substituted		925 \pm 16	887 \pm 6	858 \pm 11	824 \pm 9	763 \pm 3	
All cinnolines		924 \pm 13	889 \pm 8		816 \pm 12	777 \pm 16	

(a) Key to abbreviations and symbols: - signifies band is missing; (-) signifies band is masked by stronger absorption; (1560) signifies band at 1560 cm^{-1} appears as a shoulder and intensity is not given; s = strong; m = medium; w = weak.

band at 1025 cm^{-1} (6). The eight bands in the $1600 - 1350\text{ cm}^{-1}$ region have also been observed for other bicyclic aromatic systems such as quinolines (7) and quinoxalines (8).

The accuracy of the determination of the band frequencies in this region is somewhat low (9), therefore, it is unrealistic to discuss details in the variation of the position of the bands. However, some trends are apparent. A comparison of the mean values in table I with the mean values reported by Katritzky and Jones (7) for quinolines show that the mean frequency of the individual bands is somewhat lower for the cinnolines. The mean frequencies of the bands in substituted quinoxalines (8) are approximately the same as the ones found for the cinnolines. This decrease in the frequency of the ring stretching bands by the insertion of an extra nitrogen atom in the ring is also found when spectra of substituted pyridines and pyridazines (10) are compared.

In the 4-hydroxy- and 4-mercaptocinnolines a fairly regular decrease in frequency is observed with a change in substitution from fluorine to chlorine to bromine. A similar regular frequency shift connected with the replacement of an oxygen atom with a sulfur atom in the 4-position is not observed.

As reported for other cinnoline derivatives (2) the third band (at $1555 \pm 7\text{ cm}^{-1}$) is in general the strongest of the eight ring stretching bands. It has been reported (11) that the NH bending vibration in various α - and γ -mercapto-N-heteroaromatics gives rise to a band at $1580 - 1570\text{ cm}^{-1}$. The investigation of the spectra of the 4-mercaptocinnolines has not given any reason for making such an assignment, unless the third - very intense - ring stretching band should be considered as a superposition of the NH bending vibration and a ring stretching mode. This band was, however, also reported as being very intense for cinnolines (2) where no NH group was present.

The carbonyl stretching band of the 4-hydroxycinnolines is found at $1565 - 1615\text{ cm}^{-1}$. The values listed in table III for this absorption are chosen as the center of the strongest and broadest band in this region. In several instances two values are listed, where it has been impossible to distinguish between the carbonyl band and a ring stretching band. The figures listed for the carbonyl absorption band are thus rather uncertain, but they seem to be much lower than generally found for α - and γ -hydroxy-N-heteroaromatics (12). Mason (12) assigns a strong band at 1610 cm^{-1} to the carbonyl stretching mode in 4-hydroxycinnoline (reported at 1638 cm^{-1} in chloroform solution). The carbonyl group in the "4-hydroxy" compound is assumed to be hydrogen bonded. This normally causes a shift of the band to lower frequencies compared to a non-bonded carbonyl as in the N-methyl derivative. We prefer the value 1570 cm^{-1} for the $\nu\text{ C=O}$ band for two reasons: (a) the band at highest frequency (1604 cm^{-1}) in this region only appears as a shoulder of a much stronger band, and (b) we find a corresponding band at 1610 cm^{-1} in 4-mercaptocinnoline.

The $1350 - 1000\text{ cm}^{-1}$ Region.

The large number of bands occurring between 1350 and 1000 cm^{-1} makes the interpretation of this region somewhat difficult. In addition to the C=S stretching band and bands arising from the halogen substituents, seven or eight other bands are found. These bands are all considered to be characteristic of the ring system and are listed in table II.

Four of these bands can theoretically be accounted for as being due to CH in-plane bending vibrations, (five for unsubstituted 4-hydroxy- and 4-mercaptocinnoline). Of the bands listed in table II the one of highest frequency ($1320 \pm 7\text{ cm}^{-1}$ for the mercaptocinnolines and $1293 \pm 6\text{ cm}^{-1}$ for the hydroxycinnolines) might be assigned to a skeleton distortion mode in agreement with the assignment for a corresponding band in naphthalene (6). This assignment is based on the different position of the band for 4-hydroxycinnolines and 4-mercaptocinnolines, respectively, since it is believed that the substitution of oxygen with sulfur in the carbonyl group will influence a vibration of predominantly skeleton character more than a vibration of predominantly CH character. Another possibility is to assign this band to the ninth ring stretching mode, since some authors (13) expect to find all nine ring stretching bands in the $1600 - 1300\text{ cm}^{-1}$ region. This assignment would not be in agreement with observations made by Katritzky and Jones (7) and Cheeseman *et al.*, (8), who find only eight ring stretching bands in this region. Neither would it be in agreement with Mitra and Bernstein (6), who, as already mentioned, assign this band to a skeleton distortion mode and assign the ninth ring stretching mode to a band at 1025 cm^{-1} . In agreement with this we assign a band at *ca.* 1015 cm^{-1} to the ninth ring stretching mode. This band is often missing from the spectrum of the cinnolines, and when present is often weak.

The remaining five to six bands in $1350 - 1000\text{ cm}^{-1}$ region are assigned to the CH in-plane bending vibrations, taking into account that some of the weaker bands might be combination and overtone bands.

Several authors (7, 8, 14) report ranges for the β CH bands depending on the number and positions of hydrogens in naphthalene type aromatic systems, but these ranges overlap strongly in many instances. The β CH bands are thus of little value in structural determination where the position of a substituent is in question. As can be seen from table II this is even more apparent for the 4-hydroxy- and 4-mercaptocinnolines. One band ($1130 \pm 8\text{ cm}^{-1}$) shows some dependence on substitution, since it does not seem to be present when the cinnolines are substituted in the 5- and 8-position. The close proximity of neighboring bands and the fact that in some instances these appear as doublets, makes the absence of the 1130 cm^{-1} band in the case of 5- and 8-substituted 4-hydroxy- and 4-mercaptocinnolines somewhat uncertain.

The frequency of the band at $1225 \pm 14\text{ cm}^{-1}$ is low for 5-substituted derivatives, and the band seems

to be missing when there are four adjacent hydrogens, as in unsubstituted 4-hydroxy- and 4-mercaptocinnoline. Except in these cases the position of the β CH bands is independent of the position of the substituent. It has been demonstrated (7, 8, 14) that the vibrations of the hydrogens in the two different rings of a bicyclic system can be treated separately, since coupling is of minor importance. Consequently, Cheeseman *et al.*, (8) assigned a band at 1217 - 1199 cm^{-1} to the in-plane vibration of the 3-hydrogen in 2'-substituted quinoxalines. Hawkins *et al.*, (14) found two bands at 1223 - 1188 cm^{-1} and at 1075 - 1040 cm^{-1} to be characteristic of substituted naphthalenes with only one hydrogen left in one of the rings. However, similar ranges have been found for ring systems with four, three and two adjacent hydrogens, and the characteristics of the β CH bands found in the cinnolines does not allow us to assign any particular one of the β CH bands to the vibration of the hydrogen in the 3-position.

The other bands found in the 1350 - 1000 cm^{-1} region have been assigned to the C=S stretching vibration and to a vibration involving the halogen substituents.

It has long been generally accepted that N-heteroaromatics with a mercapto group α or γ to a ring nitrogen exist as the thione tautomers. For 4-mercaptocinnoline this was clearly demonstrated by Albert and Barlin (15) who, from ultraviolet data, calculated the thione:thiol ratio to be of the order of 90,000:1 in aqueous solution. There was of course no reason to expect that the 4-mercaptocinnolines substituted with halogens in the benzenoid part of the cinnoline system should behave differently and the presence of the broad ν NH band at 3250 - 2500 cm^{-1} and the absence of a weak ν SH band at 2600 cm^{-1} confirm that the halogen substituted 4-mercaptocinnolines are indeed the thione tautomers in the solid state.

The presence of a thiocarbonyl group should therefore give rise to a C=S stretching band in the region 1180 - 1080 cm^{-1} (11). The presence of several strong bands in this region makes the identification of the ν C=S band difficult, but it is believed that a band occurring at $1171 \pm 9 \text{ cm}^{-1}$ in the spectra of the mercaptocinnolines, which cannot be found in the spectra of the hydroxycinnolines, must be the ν C=S band. This band is listed in table III and it will be noticed that the band is missing in the spectrum of 6-fluoromercaptocinnoline. There is no reason to believe that the intensity of the ν C=S band in this compound should have decreased to such an extent as to make the band disappear. Other strong bands in the region can be satisfactorily assigned and corresponding bands occur in the spectrum of 6-fluoro-4-hydroxycinnoline. Perhaps the absence of the band should be explained by Fermi resonance resulting in a splitting of the band.

Other strong bands in the region 1200 - 1000 cm^{-1} have been assigned to vibrations involving the halogen substituents. Katritzky and Lagowski (16) found that many aromatic and heteroaromatic compounds containing halogens directly attached to the aromatic

nucleus showed characteristic absorption bands in the 1100 cm^{-1} region. These bands are believed to be due to modes involving considerable motion of both the halogen atoms and the aromatic skeleton.

For benzenes Katritzky and Lagowski (16) found bands in the spectra of substituted benzenes between *ca.* 1110 and 1020 cm^{-1} . Chlorobenzenes absorbed at higher frequency than bromobenzenes, and the frequency decreased in the order $p > m > o$, depending on the position of a second substituent. The halogen bands in chloro- and bromopyridines were shifted to higher frequencies, in the region *ca.* 1130 - *ca.* 1085 cm^{-1} . Corresponding bands were found in the spectra of the 4-hydroxy- and 4-mercaptocinnolines. These bands are listed in table III. It will be seen that the frequency of these bands vary rather strongly with the position of the substituent as was found by Katritzky and Lagowski (16).

Of the rather large number of references on infrared absorption of fluorine containing molecules, by far the most deal with aliphatic fluoro compounds. The presence of a single C-F linkage usually gives rise to a band of medium intensity in the 1100 - 1000 cm^{-1} region, but C-F stretching bands have been found over a wide range (1400 - 1000 cm^{-1}) (17). In the case of the fluorocinnolines it is suggested that the fluorine bands be assigned to a mode similar to that responsible for the chlorine and bromine bands, that is, a vibration of both the C-F bond and the ring skeleton. The spectra of the fluorine substituted 4-hydroxy- and 4-mercaptocinnolines contain a strong band at 1210 - 1165 cm^{-1} , which cannot be found in the spectra of the chlorine and bromine derivatives. This band is listed in table III and has been assigned to the ring-fluorine stretching vibration, since it seems reasonable to expect a band of this origin will lie at somewhat higher frequency than the corresponding chlorine and bromine bands.

The 1000 - 750 cm^{-1} Region.

The spectra of the 4-hydroxy- and 4-mercaptocinnolines contain approximately five bands in the region of CH out-of-plane bendings, three of which show the expected variation in frequency with the position of the substituent. These bands are listed in table IV. It will be seen that a band of medium to weak intensity occurs at $970 \pm 8 \text{ cm}^{-1}$ in the spectra of the 5- and 8-substituted derivatives and of 4-hydroxy- and 4-mercaptocinnoline themselves, which cannot be found in the spectra of the 6- and 7-substituted derivatives. The only compound in the latter group that contains a band in this region is 6-chloro-4-mercaptocinnoline, the spectrum of which contains a weak doublet at 951 and 945 cm^{-1} . The spectra of the 6- and 7-substituted derivatives on the other hand show an absorption band at $858 \pm 11 \text{ cm}^{-1}$. The bands listed in the fifth and sixth columns of table IV show a difference in frequency for 5- and 8-substituted compounds on one side and for 6- and 7-substituted compounds on the other as can be seen from the mean values listed in the table. Therefore, these bands and those at $970 \pm 8 \text{ cm}^{-1}$ and $858 \pm 11 \text{ cm}^{-1}$ have been assigned to the out-of-plane vibrations

of the hydrogens in the benzenoid part of the cinnoline system.

The band at $924 \pm 13 \text{ cm}^{-1}$ resembles a band of predominantly skeleton vibration character. The frequency of this band is extremely sensitive to variation in the halogen substituent, (mean value for fluorine derivatives, 940 cm^{-1} ; for chlorine derivatives, 923 cm^{-1} ; and for bromine derivatives, 913 cm^{-1}), whereas dependence on the position of substitution is much less evident. The characteristics of the band are thus quite different from those of the bands discussed above, and we therefore prefer to assign this band to a skeleton distortion mode. Mitra and Bernstein (6) give a band at 877 cm^{-1} in the spectrum of naphthalene a similar assignment.

In contrast the band at $889 \pm 8 \text{ cm}^{-1}$ shows no distinct variation in frequency with either position or type of substituent. The band, which often appears as a doublet, falls within the range quoted by several authors for out-of-plane bending of an isolated hydrogen atom in one of the rings of a bicyclic aromatic system. Hawkins *et al.*, (8) assigned a corresponding band at $923 - 885 \text{ cm}^{-1}$ to the vibration of the hydrogen in the 3-position of 2-substituted quinoxalines and Karr *et al.*, (18) observed bands between 885 and 856 cm^{-1} in the spectra of polymethyl substituted quinolines with an isolated hydrogen in the 3-position. Perkampus and Roders (19) reported the presence of two bands in this region in the spectra of three 2-substituted quinoxalines. On the basis of these findings it seems reasonable to assign the band at $889 \pm 8 \text{ cm}^{-1}$ in the spectra of the 4-hydroxy- and 4-mercaptocinnolines to the γ CH vibration of the hydrogen in the 3-position.

In the last column of table IV is listed a band which cannot be accounted for by γ CH vibrations. The band appears around 800 cm^{-1} and is of varying intensity, but always very broad. When present, this band lies at higher frequencies in the spectra of the hydroxycinnolines than in the spectra of the mercaptocinnolines. In several instances the band may be masked by intense γ CH absorptions and can sometimes be recognized as a broad shoulder on one of these bands. Nakamura (20) assigned the γ NH mode to this region, and it seems reasonable to assign the observed band to an NH deformation mode. Its different position for hydroxy- and mercaptocinnolines can be explained by the difference in environment in the intermolecular hydrogen bonding to a carbonyl or thiocarbonyl group.

The $750 - 400 \text{ cm}^{-1}$ Region.

An analysis of the high frequency part of the skeleton distortion and bending region between *ca.* 750 cm^{-1} and 400 cm^{-1} proved extremely difficult. We shall therefore refrain from attempting to make any

correlations between the observed bands and specific vibrations, and instead illustrate this region in Figure I, wherein the bands are pictured as lines. The height of the lines give the approximate intensity of the bands.

In this region, the spectra of the chloro and bromo-4-hydroxycinnolines are very similar when substituted with halogen in the same position, however the spectra of the corresponding fluoro derivatives are somewhat different. Several of the bands in this region (Figure I) show the characteristic decrease in frequency by changing the substituent from fluorine to chlorine to bromine in the 4-hydroxycinnolines.

A comparison of the spectra of the halogen-substituted 4-hydroxycinnolines with the spectra of the corresponding halogen-substituted 4-mercaptocinnolines reveals very few similarities.

In a complete analysis of the infrared and Raman spectrum of naphthalene Mitra and Bernstein (6) list eight bands in the region $750 - 400 \text{ cm}^{-1}$. The number of bands found in the spectra of the hydroxy- and mercaptocinnolines vary from six to ten.

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