

**594.** *The Infrared Spectra of Polycyclic Heteroaromatic Compounds. Part I. Monosubstituted Quinolines.*

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The bands characteristic of the various mono-substituted quinoline nuclei are correlated with those of similarly substituted naphthalenes, and tentative assignments to specific molecular vibration modes are suggested.

THE infrared bands ( $\epsilon_A \geq 15$ ) for monosubstituted benzenes, pyridines, pyridine 1-oxides, furans, and thiophenes are characteristic of either the substituent or the nucleus.<sup>1</sup> Further, any one nucleus (or substituent) shows a definite number of bands, the positions and intensities of which are either reasonably constant or vary with the electronic nature of the substituent (or nucleus); mass effects are small provided the substituent is attached to the nucleus by a carbon, nitrogen, or oxygen atom. We are now investigating polycyclic compounds, and this paper describes the results for monosubstituted quinolines. For

<sup>1</sup> For references see Katritzky, *Quart. Rev.*, 1959, **13**, 353.

reasons already given,<sup>2</sup> where possible, the spectra of 0.189M-chloroform solutions were measured in a 0.106 mm. compensated cell and apparent molecular extinction coefficients measured; the errors and approximations involved are noted in ref. 2. As in our earlier work the bands were characteristic of the ring or of the substituent. The bands characteristic of each class of substituted quinoline were recorded for the following compounds: 2-amino-, -ethoxycarbonylamino-, -methoxy-, -chloro-, -methyl-, -2'-hydroxyethyl-, and -methoxycarbonyl-quinoline; 3-amino-, -acetamido-, -bromo-, -methyl-, -cyano-, -ethoxycarbonyl-, and -nitro-quinoline; 4-amino-, -anilino-, -acetamido-, -methyl-, -cyano-, -carbamoyl-, -formyl-, -methoxycarbonyl-, and -nitro-quinoline; 5-amino-, -thioformamido-, -methoxy-, -hydroxy-, -methyl-, and -nitro-quinoline; 6-amino-, -acetamido-, -chloro-, -methyl-, -formyl-, -methoxycarbonyl-, and -nitro-quinoline; 7-chloro-, -methyl-, -ethoxycarbonyl-, and -nitro-quinoline; 8-amino-, -thioformamido-, -hydroxy-, -chloro-, -methyl-, -methoxycarbonyl-, and -nitro-quinoline.

In our work on monocyclic heterocyclic compounds we found that the number and position of the ring stretching bands in the 1600—1400  $\text{cm}^{-1}$  region were not very sensitive to the orientation or the nature of the substituents, but that the intensity of these bands was often altered drastically. However, the number and position of the CH in-plane and CH out-of-plane deformation bands depended on the number and orientation of the substituents. The data now obtained lead to similar conclusions for the quinolines, as discussed below. In our work on the monocyclic compounds, we were helped by the assignments Randle and Whiffen<sup>3</sup> made for the bands for substituted benzenes; we have been aided in the present work by Hawkins, Ward, and Whiffen's study of naphthalenes.<sup>4</sup>

The infrared and Raman spectra of quinoline itself have been discussed in detail by Chiorboli and Bertoluzza<sup>5</sup> who have made a nearly complete assignment based on naphthalene.

**Ring-stretching Bands in the 1620—1560  $\text{cm}^{-1}$  Region.**—The results are summarised in Table I. Three bands are usually found, near 1620, 1590, and 1575  $\text{cm}^{-1}$ , and these

TABLE I. Ring-stretching bands at 1620—1560  $\text{cm}^{-1}$ .\*

Posn. of substn.	First band		Second band		Third band	
	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$
None	1622	25	1598	35	1576	40
2-	{ 1622 $\pm$ 2 1608 $\pm$ 3 1617 $\pm$ 3 }	250 $\longrightarrow$ 10 340 $\longrightarrow$ <10 15 $\longrightarrow$ 150	1588 $\pm$ 6	165 $\longrightarrow$ 20	1570 $\pm$ 4	85 $\longrightarrow$ 25
3-	1617 $\pm$ 3	15 $\longrightarrow$ 150	ca. 1605	ca. 35	1578 $\pm$ 6	25 $\longrightarrow$ 90
4-	1617 $\pm$ 2	10 $\pm$ 5	1592 $\pm$ 6	180 $\longrightarrow$ 55	1573 $\pm$ 3	145 $\longrightarrow$ 20
5-	1621 $\pm$ 4	—	1593 $\pm$ 5	190 $\longrightarrow$ 40	1575 $\pm$ 7	135 $\longrightarrow$ 35
6-	1622 $\pm$ 3	80 $\longrightarrow$ 10 $\longrightarrow$ 150	1599 $\pm$ 5	50 $\pm$ 25	1575 $\pm$ 3	30 $\pm$ 15
7-	1621 $\pm$ 6	40 $\pm$ 30	1595 $\pm$ 5	50 $\pm$ 15	1570 $\pm$ 7	30 $\pm$ 5
8-	1619 $\pm$ 6	20 $\pm$ 5	1597 $\pm$ 1	145 $\longrightarrow$ 40	1579 $\pm$ 3	50 $\pm$ 25
All subst.	1623 $\pm$ 5	50 $\pm$ 50	1598 $\pm$ 8	75 $\pm$ 45	1577 $\pm$ 6	55 $\pm$ 35

\* Arithmetical means and standard deviations given.

250  $\longrightarrow$  10 means that the absorption depends upon the electronic properties of the substituent in such a way that it falls from ca. 250 for strong electron-donors to ca. 10 for strong electron-acceptors.

positions do not vary greatly (however, 2-substituted quinolines show four bands) Chiorboli and Bertoluzza's<sup>5</sup> work would indicate that modes (I), (II) and (III), and (IV), respectively, were the origin of these bands. The intensity of the first band is low for the 4-, 5-, and 8-substituted compounds; it rises for the 3- and falls for the 2- and 7-substituted

<sup>2</sup> Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

<sup>3</sup> Randle and Whiffen, Paper No. 12, Report on the Conference of Molecular Spectroscopy, Institute of Petroleum, 1954.

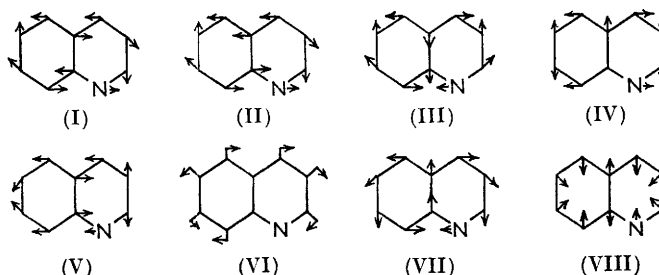
<sup>4</sup> Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105.

<sup>5</sup> Chiorboli and Bertoluzza, *Ann. Chim. (Italy)*, 1959, **49**, 245.

quinolines with increasing electron-accepting power of the substituent and shows a more complicated dependence for the 6-isomers.

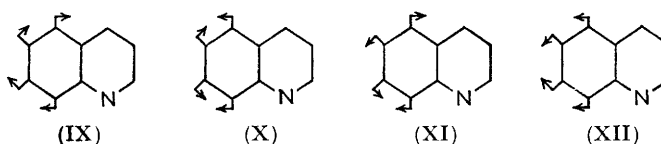
**Ring-stretching Bands in the 1500—1350  $\text{cm}^{-1}$  Region** (Table 2).—Five bands are usually found, near 1500, 1470, 1440, 1400, and 1360  $\text{cm}^{-1}$ ; again, these positions are relatively invariant. The apparent extinction coefficient for the first band is near 100 for the 3-, 4-, 7-, and 8-compounds, and low for the 5-isomers, and it falls with decreasing donor power of the substituent for the 2- and 6-substituted compounds.

The second, third, fourth, and fifth bands frequently have  $\epsilon_A$  values of *ca.* 20—40. However, the intensity of the second band falls with decreasing electron-donor properties of the substituent for 5- and 8-substituted compounds and falls and then rises for the



corresponding 2-isomers. The third band is absent for 5-substituted compounds and the intensity falls with decreasing electron-donor properties of the substituent for the 2-, 3-, and 4-compounds. The fourth band is absent for the 8-isomers, and is of high intensity for 5-substituted compounds.

Chiorboli and Bertoluzza<sup>5</sup> assigned bands at 1499, 1430, 1400, and 1360  $\text{cm}^{-1}$  in



quinoline to modes (V)—(VIII) respectively. Three of these bands correspond to the first, to the third, and to the fifth of our sequences. However, the 1430  $\text{cm}^{-1}$  band is at a very high frequency for a CH in-plane vibration (VI), and finding this sequence throughout the various substituted compounds causes us to reject this assignment.

**In- and Out-of-plane CH-Deformation Frequencies in the 1300—800  $\text{cm}^{-1}$  Region.**—By analogy with the similarities found between bands of this type in monosubstituted pyridines with those in benzenes,<sup>1</sup> absorption of the quinolines in this region should be comparable to that of corresponding naphthalenes. Whiffen and his co-workers have shown<sup>4</sup> that the characteristic absorption pattern of naphthalenes in this region could be correlated with the substitution pattern, each ring being treated separately. They

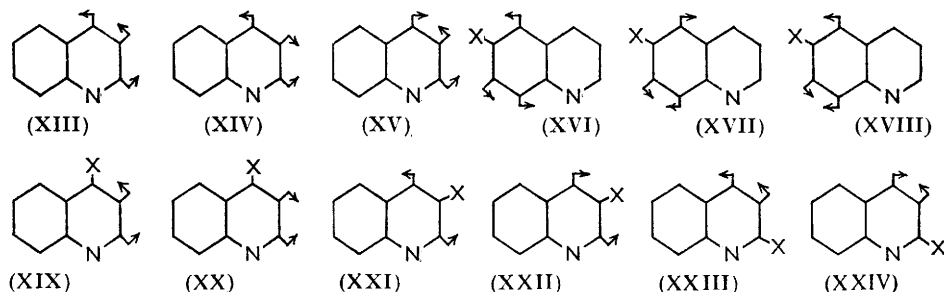


TABLE 2. Ring-stretching bands in the 1500—1350  $\text{cm}^{-1}$  region.

Posn. of substn. $\text{C}^1$	First band		Second band		Third band		Fourth band		Fifth band	
	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$
None	1506	110	{ 1473 1453	10	1435	15	1396	15	1374	25
2-	1508 $\pm$ 4	150 $\longrightarrow$ 20	1473 $\pm$ 13	240 $\longrightarrow$ 10	1428 $\pm$ 6	370 $\longrightarrow$ 25	1380 $\pm$ 16	65 $\pm$ 50	1344 $\pm$ 8	20 $\pm$ 15
3-	1500 $\pm$ 4	80 $\pm$ 15	1469 $\pm$ 7	35 $\pm$ 20	1448 $\pm$ 9	80 $\longrightarrow$ 10	1420 $\pm$ 6	ca. 15	1374 $\pm$ 10	30 $\longrightarrow$ 90
4-	1507 $\pm$ 7	80 $\pm$ 60	1465 $\pm$ 5	35 $\pm$ 15	1444 $\longrightarrow$ 1405	85 $\longrightarrow$ 10	1395 $\pm$ 6	ca. 40	1361 $\pm$ 8	45 $\pm$ 25
5-	1504 $\pm$ 6	ca. 25	1469 $\pm$ 7	75 $\longrightarrow$ 10	—	—	1417 $\pm$ 10	95 $\pm$ 30	1372 $\pm$ 4	45 $\pm$ 20
6-	1502 $\pm$ 5	200 $\longrightarrow$ 30 <sup>a</sup>	1466 $\pm$ 6	60 $\pm$ 50	1439 $\pm$ 10	35 $\pm$ 20	1376 $\pm$ 10	40 $\pm$ 25	1348 $\pm$ 7	ca. 30
7-	1499 $\pm$ 5	80 $\pm$ 45	ca. 1445	ca. 15	ca. 1435	ca. 15	1385 $\pm$ 5	ca. 20	ca. 1350	ca. 10
8-	1501 $\pm$ 5	125 $\pm$ 60	1471 $\pm$ 6	60 $\longrightarrow$ 10	1430 $\pm$ 8	15 $\pm$ 5	1383 $\pm$ 10	80 $\pm$ 70	ca. 1355	ca. 20
All subst.	1503 $\pm$ 6	95 $\pm$ 50	1466 $\pm$ 8	50 $\pm$ 50	1433 $\pm$ 11	50 $\pm$ 50	1388 $\pm$ 19	50 $\pm$ 50	1358 $\pm$ 14	35 $\pm$ 25

<sup>a</sup> Intensity of nitro-compound (240) excepted.

TABLE 3. Four hydrogen atoms at 5, 6, 7, 8.

	(IX)		(X)		(XI)		(XII)		$\gamma_{\text{CH}}$	
	$\beta_{\text{CH}}$	$\epsilon_A$	$\beta_{\text{CH}}$	$\epsilon_A$	$\beta_{\text{CH}}$	$\epsilon_A$	$\beta_{\text{CH}}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$
<i>ortho</i> -Disubst. benzenes <sup>b</sup>	1269 $\pm$ 17	15 $\pm$ 5	1160 $\pm$ 4	20 $\pm$ 10	1125 $\pm$ 14	25 $\pm$ 15	1040 $\pm$ 6	50 $\pm$ 40	948 $\pm$ 7	10 $\longrightarrow$ 15
Naphthalenes <sup>c</sup>	1269 $\pm$ 8	m-s	1239 $\pm$ 9	var.	1137 $\pm$ 10	w-m	1028 $\pm$ 10	var.	957 $\pm$ 8	m
2-Subst. quinolines	1302 $\pm$ 11	40 $\pm$ 25	1254 $\pm$ 10	25 $\pm$ 10	1115 $\pm$ 5	50 $\pm$ 25	ca. 1015	$\leq$ 10	970 $\pm$ 4	10 $\pm$ 5
3-Subst. quinolines	1257 $\pm$ 4	25 $\pm$ 10	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1142 $\pm$ 4	25 $\pm$ 5	1015 $\pm$ 2	15 $\pm$ 5	960 $\pm$ 8	30 $\pm$ 15
4-Subst. quinolines	1294 $\pm$ 12	25 $\pm$ 10	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1143 $\pm$ 3	20 $\pm$ 10	1027 $\pm$ 16	30 $\pm$ 30	953 $\pm$ 5	ca. 15
Quinolines	1315	40	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1141	20	1035	20	940	25

Arithmetical means and standard deviations given in all tables. Roman numerals refer to diagrams.

<sup>a</sup> Intensities of chloro- (120) and aldehyde- (95) compounds excepted.<sup>b</sup> See ref. 10. <sup>c</sup> See ref. 4.

TABLE 4. Three hydrogen atoms at 2, 3, 4 (also 5, 6, 7 and 6, 7, 8).

	(XIII)		(XIV)		(XV)		Ring?		$\gamma_{\text{CH}}$	
	$\beta_{\text{CH}}$	$\epsilon_A$	$\beta_{\text{CH}}$	$\epsilon_A$	$\beta_{\text{CH}}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$	$\text{cm}^{-1}$	$\epsilon_A$
1,2,3-Trisubst. benzenes <sup>d</sup>	1214 $\pm$ 10	?	1160 $\pm$ 5	1073 $\pm$ 10	1073 $\pm$ 10	s	1017 $\pm$ 6	770 $\pm$ 8	770 $\pm$ 8	vs
Naphthalenes <sup>c</sup>	(CHCl <sub>3</sub> )	Var.	1170 $\pm$ 8	1077 $\pm$ 8	1077 $\pm$ 8	w-m	—	795 $\pm$ 9	795 $\pm$ 9	s
5-Subst. quinolines	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1142 $\pm$ 8	30 $\pm$ 25	1071 $\pm$ 8	25 $\pm$ 20	1043 $\pm$ 9	10 $\pm$ 5	817 $\pm$ 11	50 $\pm$ 35
6-Subst. quinolines	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1145 $\pm$ 3	15 $\pm$ 5	—	—	1033 $\pm$ 6	20 $\pm$ 10	(—)	(—)
7-Subst. quinolines	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1139 $\pm$ 6	ca. 25	1069 $\pm$ 4	45 $\pm$ 25	1034 $\pm$ 4	ca. 20	—	—
8-Subst. quinolines	1304 $\pm$ 18	30 $\pm$ 20	1131 $\pm$ 4	20 $\pm$ 10	1069 $\pm$ 12	25 $\pm$ 15	—	822 $\pm$ 5	110 $\pm$ 40	25
Quinoline	(CHCl <sub>3</sub> )	(CHCl <sub>3</sub> )	1121	45	1093	5	1014	10	820 <sup>*</sup>	—

<sup>a</sup> Ref. 4. <sup>d</sup> Ref. 3. <sup>\*</sup> Shoulder.

2946 *Infrared Spectra of Polycyclic Heteroaromatic Compounds. Part I.*TABLE 5. *Three hydrogen atoms at 5,6,8 and 5,7,8.*

	$\beta_{\text{CH}}$ (XVI)		$\beta_{\text{CH}}$ (XVII)		Ring?	
	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$
1,2,4-Trisubst. benzenes <sup>d</sup> ...	1151 $\pm$ 8	m	1127 $\pm$ 10	m	1004 $\pm$ 7	Var.
Naphthalenes <sup>e</sup> .....	1180 $\pm$ 10	Var.	1092 $\pm$ 12	m-s	972 $\pm$ 9	m
6-Subst. quinolines .....	1172 $\pm$ 11	25 $\pm$ 15	1120 $\pm$ 2	60 $\pm$ 25	976 $\pm$ 3	15 $\pm$ 5
7-Subst. quinolines .....	—	—	—	—	945 $\pm$ 4	25 $\pm$ 10

	$\gamma_{\text{CH}}$		$\gamma_{\text{CH}}$		$\gamma_{\text{CH}}$	
	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$
1,2,4-Trisubst. benzenes <sup>d</sup> ...	929 $\pm$ 11	w	868 $\pm$ 11	w	816 $\pm$ 14	vs
Naphthalenes <sup>e</sup> .....	901 $\pm$ 10	m-s	864 $\pm$ 10	m-s	824 $\pm$ 12	vs
6-Subst. quinolines .....	893 $\pm$ 12	55 $\pm$ 30	858 $\pm$ 14	75 $\pm$ 40	829 $\pm$ 1	165 $\pm$ 50
7-Subst. quinolines .....	891 $\pm$ 17	70 $\pm$ 40	—	—	834 $\pm$ 6	125 $\pm$ 30

<sup>e</sup> Ref. 4. <sup>d</sup> Ref. 3.

TABLE 6. *Two hydrogen atoms at 2,3.*

	?		$\beta_{\text{CH}}$ (XIX)		$\beta_{\text{CH}}$ (XX)		$\gamma_{\text{CH}}$	
	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$
1,2,3,4-Tetrasubst. benzenes <sup>d</sup>	—	—	—	—	1165	s	804	vs
Naphthalenes <sup>e</sup> .....	1263 $\pm$ 11	Var.	1193 $\pm$ 6	m-s	1160 $\pm$ 7	Var.	824 $\pm$ 6	s-vs
4-Subst. quinolines .....	—	—	—	—	1161 $\pm$ 3	25 $\pm$ 15	849 $\pm$ 8	70 $\pm$ 40

<sup>e</sup> Ref. 4. <sup>d</sup> Ref. 3.

TABLE 7. *Two hydrogen atoms at 2,4.*

	$\beta_{\text{CH}}$ (XXI)		$\beta_{\text{CH}}$ (XXII)		$\gamma_{\text{CH}}$ out-of-phase		$\gamma_{\text{CH}}$ in-phase	
	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$
1,2,3,5-Tetrasubst. benzenes <sup>d</sup> .....	1161	Var.	—	—	—	—	851	vs
Naphthalenes <sup>e</sup> .....	1204 $\pm$ 6	Var.	1102 $\pm$ 9	Var.	888 $\pm$ 10	m-s	861 $\pm$ 8	s
3-Subst. quinolines .....	1179 $\pm$ 9	ca. 30	1099 $\pm$ 17	ca. 30	890 $\pm$ 10	65 $\pm$ 45	854 $\pm$ 8	50 $\pm$ 35

TABLE 8. *Two hydrogen atoms at 3,4.*

	$\beta_{\text{CH}}$ (XXIII)		$\beta_{\text{CH}}$ (XXIV)		$\gamma_{\text{CH}}$ out-of-phase		$\gamma_{\text{CH}}$ in-phase	
	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$	cm. <sup>-1</sup>	$\epsilon_{\text{A}}$
1,2,3,4-Tetrasubst. benzenes <sup>d</sup> .....	—	—	1165	s	—	—	804	vs
Naphthalenes <sup>e</sup> .....	1220 $\pm$ 5	Var.	1151 $\pm$ 5	m	940 $\pm$ 14	w	810 $\pm$ 10	s
2-Subst. quinolines .....	(CHCl <sub>3</sub> )	—	1141 $\pm$ 3	30 $\pm$ 10	945 $\pm$ 4	ca. 20 <sup>a</sup>	822 $\pm$ 10	160 $\pm$ 60

<sup>a</sup> Intensity of the chloro-compound excepted. <sup>c, d</sup> See earlier Tables.

suggested no assignments for these bands, but as each ring could be treated separately an attempt has now been made to correlate these bands with the correlations for similarly substituted (monocyclic) benzenes established by Randle and Whiffen.<sup>3</sup> The data for similarly substituted benzenes, naphthalenes, and quinolines are arranged in Tables 3—8 to bring out these relations. Of 53 band sequences found in this region for the quinolines, it was possible to correlate 46 with the naphthalenes and benzenes as detailed:

Position of substituent in quinoline .....	2	3	4	5	6	7	8
Total no. of bands between 1300—800 cm. <sup>-1</sup> .....	9	11	8	5	9	6	5
No. correlated in Tables 3—8 .....	9	8 <sup>a</sup>	7 <sup>b</sup>	4 <sup>c</sup>	8 <sup>d</sup>	6	4 <sup>e</sup>

Additional band sequences at: <sup>a</sup> 1127  $\pm$  3 (30  $\pm$  15); 980  $\pm$  6 (30  $\pm$  10); and 935  $\pm$  9 (80  $\pm$  40); <sup>b</sup> 1088  $\pm$  18 (55  $\pm$  40); <sup>c</sup> 1001  $\pm$  17 (ca. 10); <sup>d</sup> 950  $\pm$  5 (10  $\pm$  5); <sup>e</sup> 866  $\pm$  25 (20  $\pm$  5).

Bands corresponding to some modes are not found, *e.g.*, (XVIII) for 6-substituted quinolines, because they are intrinsically weak.

Previous work has been concerned mainly with the out-of-plane CH deformation modes in the region 900—700 cm.<sup>-1</sup> (which was partially obscured in our work) and has been

limited to alkylquinolines. Karr *et al.*<sup>6</sup> demonstrated that the two strongest CH out-of-plane modes (*i.e.*, the modes with all the hydrogen atoms of each ring moving in phase) of 50 mono- and poly-alkylquinolines could usually be correlated with fair accuracy with the bands of corresponding naphthalenes, benzenes, and pyridines. Shindo and Tamura<sup>7</sup> obtained the spectra of all the monomethylquinolines and reached similar conclusions; they also pointed out that methylquinolines usually showed three bands in the 1600 cm.<sup>-1</sup> region and another near 1500 cm.<sup>-1</sup>.

*Other Bands.*—The compounds showed the characteristic bands of the substituents;<sup>8</sup> very few bands (less than 2% of the whole) could be correlated with neither the ring nor the substituent.

*Experimental.*—For conditions of measurement see refs. 2 and 6. Compounds were recrystallised or redistilled immediately before measurement.

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<sup>6</sup> Karr, Estep, and Papa, *J. Amer. Chem. Soc.*, 1959, **81**, 152.

<sup>7</sup> Shindo and Tamura, *Pharm. Bull. (Japan)*, 1956, **4**, 292.

<sup>8</sup> Katritzky and his co-workers, *J.*, 1958, 2182; 1959, 2062, 2067, and in the press.

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