

701. The Infrared Spectra of Polycyclic Heteroaromatic Compounds. Part III.¹ 2-, 5-, and 6-Substituted Quinoxalines.

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The infrared spectra of quinoxaline, nine of its 2-substituted, five of its 5-substituted, and eight of its 6-substituted derivatives are recorded and discussed with tentative assignments of characteristic bands to specific molecular vibration modes.

LITTLE is known of the infrared spectra of quinoxalines (for a review of infrared spectra of heterocycles see ref. 2) with the exception of correlations established by Perkampus with Roders³ of the in-phase, out-of-plane CH bending modes. We have now investigated quinoxaline and its derivatives with the following substituents: 2-NMe₂, 2-NH₂, 2-NHAc, 2-OMe, 2-Cl, 2-Ph, 2-Me, 2-CBr₃, 2-CO₂Et; 5-NH₂, 5-NHAc, 5-OMe, 5-Cl, 5-NO₂; and 6-NH₂, 6-NHAc, 6-OMe, 6-Cl, 6-Br, 6-Ph, 6-Me, 6-NO₂.

Where possible,⁴ 0.195M-chloroform solutions in a 0.1025 mm. compensated cell were measured, and apparent extinction coefficients found; for the errors and approximations involved see ref. 4. Bands were characteristic either of the substituent or of the substituted quinoxaline ring: the ring bands were interpreted with the help of previous work on naphthalenes⁵ and quinolines.^{6,7}

Ring-stretching Bands in the 1620—1350 cm.⁻¹ Region.—All the compounds absorb at

¹ Part II, Cheeseman, Katritzky, and Øksne, *J.*, 1961, 3983.

² Katritzky and Ambler in "Physical Methods in Heterocyclic Chemistry," Academic Press, New York, 1963, Chapter 10.

³ Perkampus and Roders, *Z. Naturforsch.*, 1960, **15b**, 1.

⁴ Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

⁵ Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105.

⁶ Katritzky and Jones, *J.*, 1960, 2942.

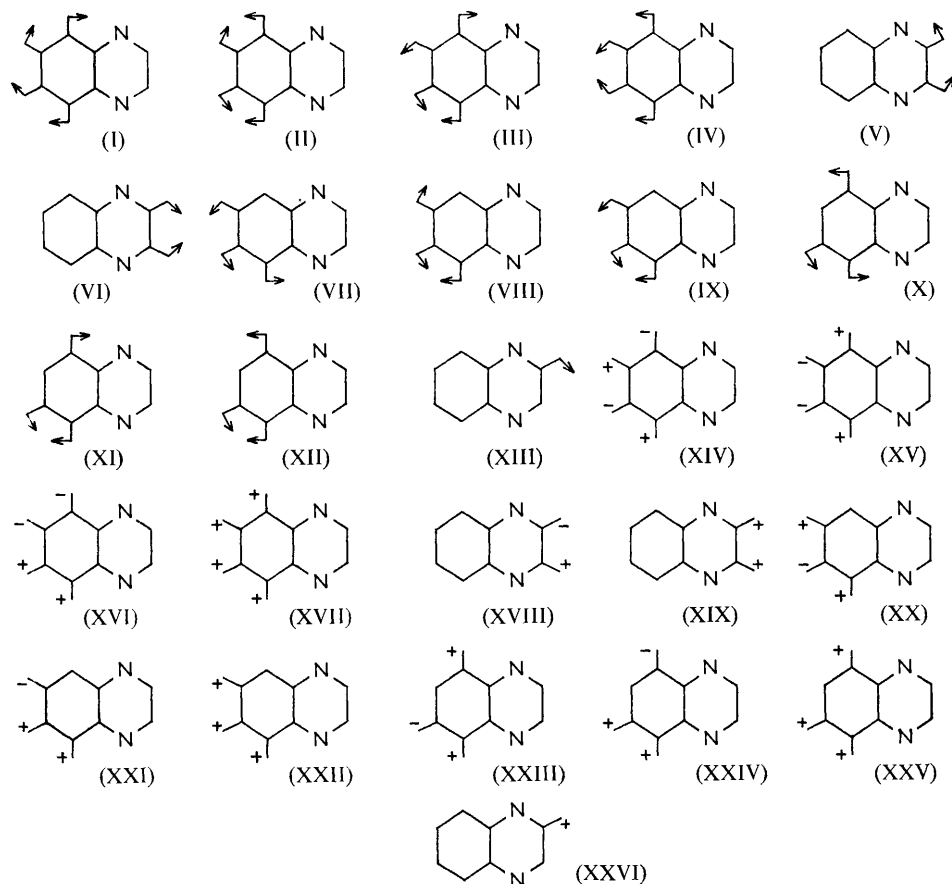
⁷ Chiorboli and Bertoluzza, *Ann. Chim. (Italy)*, 1959, **49**, 245; Luther, Mootz, and Radwitz, *J. prakt. Chem.*, 1958, **5**, 242.

1625—1600 [1614 ± 7] cm^{-1} *; this band is of low intensity in quinoxaline itself (ϵ_A 5) but rises in each series as the substituents change from electron-acceptors to electron-donors, ϵ_A 5 \rightarrow 75, 10 \rightarrow 85, and 30 \rightarrow ca. 250 for the 2-, 5-, and 6-substituted derivatives, respectively.

The 6-substituted quinoxalines absorb at 1587—1570 (10—35) [1578 ± 2 cm^{-1} (20 ± 8)] (except that the NHAc compound absorbs more intensely). In this region, 1585—1555 cm^{-1} , the 2- and 5-derivatives show a doublet or a single band of variable intensity.

All the compounds absorb at 1515—1489 [1499 ± 7] cm^{-1} ; this band is rather more intense (120—290) [210 ± 60] for the 6-substituted derivatives than for the 2- and 5-analogues (40—140) [95 ± 28], except that the 2- and 5-acetamido-compounds absorb much more strongly. Another band occurs at 1482—1450 [1468 ± 8] cm^{-1} , but its intensity is rather variable: (20—115) [55 ± 40] for 6-substituted; (70—195) [130 ± 60] for 5-substituted (except that the band is absent for the nitro-compound); and (10—20) for most 2-substituted derivatives, although much stronger for the acetamido-, methoxy-, and nitro-compounds.

A further band is found in the 1450—1400 cm^{-1} region. The frequency is higher,



1450—1422 [1439 ± 10] cm^{-1} , and the intensity lower (20—100) [55 ± 30], for 6-substituted quinoxalines than for the 5-analogues 1415—1405 cm^{-1} (10—55) [1411 ± 4 ($35 \pm$

* Parentheses indicate apparent extinction coefficients and square brackets indicate arithmetical means and standard deviations: shoulders and superposed bands are not indicated in the statistical treatment of intensities, and shoulders not in the statistical treatment of frequencies.

20)]. The band is very intense (220—390) for 2-substituents which are strong electron-donors, and weak (15—35) for other 2-substituents: the frequency lies at 1435—1400 [1418 ± 11] cm.⁻¹ for these compounds.

The seventh band is of moderate intensity (10—90) [(45 ± 20)] (except for the 5-acetamido-derivative): the frequency is 1375—1365 [1371 ± 3] cm.⁻¹ for the 2- and 6-derivatives, but significantly higher at 1391—1375 [1383 ± 7] cm.⁻¹ for 5-substituted quinoxalines. The final ring-stretching band occurs at 1365—1320 [1350 ± 13] cm.⁻¹ and is of very variable intensity (<5—230).

Substituted quinolines show eight ring-stretching bands: at 1623 ± 5, 1598 ± 8, 1577 ± 6, 1503 ± 6, 1466 ± 8, 1433 ± 11, 1388 ± 19, and 1358 ± 14 cm.⁻¹. These

Absorption of quinoxalines in the 1300—800 cm.⁻¹ region.

Assignment	Range (cm. ⁻¹)	Statistics *		Range (ε _A)	Statistics *	
<i>2-Substituted quinoxalines</i>						
β-CH I	1297—1275	1287	6	5—80	45	30
β-CH II	1270—1245	1258	10	20—115	60	40
β-CH XIII	1217—1199	1209	5	<5—100	45	—
β-CH III	1157—1128	1139	9	20—160	85	45
	1130—1121	1127	2	<5—100	45	—
β-CH IV	1025—1010	1017	4	5—55	30	20
γ-CH XIV	988—955	969	10	25—160	75	35
γ-CH XV	960—935	949	10	<5—20	15	—
γ-CH XXVI	923—885	908	10	10—110	40	30
γ-CH XVI	877—855	865	8	<5—60	25	—
<i>5-Substituted quinoxalines</i>						
?	1287—1271	1279	4	15—40	30	10
β-CH VII	1271—1217	1240	20	15—25	20	5
β-CH V, VII	1210—1185	1200	12	20—60	40	20
β-CH VI	1168—1137	1153	14	5—145	45	—
β-CH IX	1080—1060	1068	8	20—55	40	15
Ring modes ?	1040—1020	1032	8	5—105	40	—
	1007—987	997	8	20—310	80	—
γ-CH XIX	867—858	863	4	60—160	105	40
γ-CH XXII	835—825	828	4	35—140	60	—
γ-CH ?	825—813	817	5	15—35	25	5
<i>6-Substituted quinoxalines</i>						
?	1298—1273	1287	11	<5—45	20	15
β-CH V	1227—1207	1217	7	<5—250	80	—
β-CH X	1210—1167	1188	16	30—125	65	35
β-CH XI	1078—1045	1061	16	<5—90	30	—
Ring modes	1030—1018	1025	4	<5—150	75	—
	958—952	956	2	50—130	95	25
γ-CH XXIII	940—910	923	10	5—160	40	—
γ-CH XXIV	895—885	888	2	<5—330	90	—
γ-CH XIX	868—861	865	2	80—190	130	45
γ-CH	832—812	823	6	40—230	85	—

* Arithmetic mean and standard deviation.

frequencies are close to those found for the quinoxalines, indicating a similar origin. A planar aromatic ring system with ten annular atoms would be expected to show nine β ring modes in the 1650—1300 cm.⁻¹ region;⁷ one of these is presumably too weak to be detected. The intensity of the band near 1600 cm.⁻¹ might be expected to depend strongly on the electronic nature of the substituent, from the observation of the intensity pattern in monocyclic heteroaromatic rings.⁸

Absorption below 1300 cm.⁻¹.—In this region absorption due to in-plane β-CH bending modes at ca. 1300—1050 cm.⁻¹, ring breathing modes near 1000 cm.⁻¹, and out-of-plane γ-CH bending modes, is expected.

Previous work on substituted quinolines⁶ and naphthalenes⁵ showed that the two rings could be considered independently for the β-CH modes (I—XIII) and the γ-CH

⁸ Katritzky, *J.*, 1958, 4162.

modes (XIV—XXVI). Characteristic absorption bands for 2-, 5-, and 6-substituted quinoxalines are recorded in the Table. The band sequences have been tentatively assigned to modes I—XXVI (see Table) by comparison with the earlier work.^{5,6}

Quinoxaline itself absorbs at 1290 (10) (β -CH I); 1210 (*35*)[†] (β -CH, II and V?); 1133 (55) (β -CH, III); 1102 (15) (β -CH, VI); 1045* (15), 1029 (130) (ring-breathing and β -CH, IV); 955 (95) (γ -CH, XIV ?); 870 (140) (γ -CH, XIX); 756 (200) cm.^{-1} (γ -CH, XVII). The assignments suggested are tentative.

Some 5-substituted quinoxalines show weak absorption near 970 and 880 cm.^{-1} , and these bands may correspond to modes (XX) and (XXI) which absorb at 958 ± 8 w and 983 ± 7 w, respectively, for 1,2,3-trisubstituted benzenes.⁹

In Nujol mulls, 5-substituted quinoxalines show a characteristic band at 770—745, cm.^{-1} which may be a ring deformation mode: 2-substituted quinoxalines show the strong in-phase γ -CH mode (XVII) at 765—755 cm.^{-1} , and also a weak band near 790 cm.^{-1} .

Experimental.—See ref. 4 for details. Compounds were prepared by standard methods and had m. p. or b. p. (see Table) which were in agreement with the literature.

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* Shoulder.

† Italicised ϵ_A indicates estimated value from Nujol mull due to solvent absorption in solution spectrum.

⁹ Randle and Whiffen, Paper No. 12, Conference on Molecular Spectroscopy, Institute of Petroleum, 1954.
