775. *The Infrared Spectra of Polycyclic Heteroaromatic Compounds. Part II.*[1] *Quinoxaline-2,3-diones.*

By G. W. H. Cheeseman, A. R. Katritzky, and S. Øksne.

Infrared spectra confirm that tautomeric forms of the quinoxaline-2,3-dione type are more stable than those of the 3-hydroxy-2-quinoxalone or 2,3-dihydroxyquinoxaline types.

Maleic hydrazide has been shown to exist predominantly as (I), and phthalic hydrazide as (II), by various techniques.[2] Presumably this is because full conjugation in the dioxo-forms of these compounds is hindered by two electron-donor groups' being adjacent to each other; in valence-bond terms, canonical forms of type (III) are not favoured. The predominant existence in the hydroxy-form of a six-membered heterocycle with the hydroxy-group α or γ to a nitrogen atom is most unusual. The reverse situation, in which the carbonyl groups are α to each other, is thus of interest.

Cheeseman[3] compared the ultraviolet spectra of quinoxaline-2,3-dione (IV) and its

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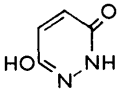
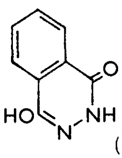
[1] Part I, Katritzky and Jones, *J.*, 1960, 2942.

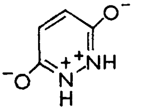
[2] See, *inter al.*, Cheinker, Gortinskaia, and Sycheva, *J. Chim. phys.*, 1958, **55**, 217; *Zhur. fiz. Khim.*, 1957, **31**, 599; Elvidge and Redman, *J.*, 1960, 1710; Miller and White, *Canad. J. Chem.*, 1956, **34**, 1510.

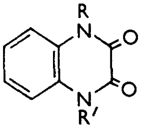
[3] Cheeseman, *J.*, 1958, 108.

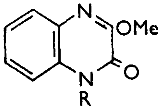
O- and *N*-methyl-derivatives; this comparison indicated that the parent compound probably existed predominantly in the dione form. This conclusion is now supported by the infrared spectra of compounds (IV)—(IX) measured as Nujol and perchlorobutadiene mulls, potassium bromide discs, and, where solubility allowed, in chloroform solution. The spectra of solutions and solids were similar, indicating that no change in the predominant tautomer occurred. The assignments in the Tables are based on previous work on *o*-disubstituted benzenes,[4] quinolines,[1] pyridones,[5] and methoxy-compounds,[6] but are very tentative because of the small number of compounds investigated, and their low solubility.

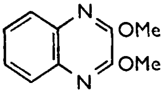

(I)


(II)


(III)


(IV) ; R = R′ = H
(V) ; R = H, R′ = Me
(VI) ; R = R′ = Me


(VII) ; R = H
(VIII) ; R = Me


(IX)

The 3000 *cm.*$^{-1}$ *Region.*—Little useful information can be obtained from this region. The potentially tautomeric compounds are very sparingly soluble in chloroform, and their solid-state spectra show a complex pattern of peaks in the range 3100—2700 cm.$^{-1}$ which would be due to either OH or NH bonds.

The 1750—1550 *cm.*$^{-1}$ *Region.*—The compounds (IV)—(VI) containing two carbonyl groups show a very strong νC=O near 1690 cm.$^{-1}$, split into two peaks. Those with one carbonyl group (VII and VIII) show a narrower single band in the same region. All the compounds show two bands near 1600 cm.$^{-1}$, one of these being very strong for the monocarbonyl compounds (see Table 1).

TABLE 1. *The* 1750—1550 *cm.*$^{-1}$ *region.*

Compd.			γC=O		Ring stretching	
(IV)	NH	NH	1712vs	1685vs	1618m	1600w
(V)	NH	NMe	1690 *	1675vs	1610m	1598m
(VI)	NMe	NMe	1708 *	1677vs	1601w	1594w
(VII)	NH	OMe	—	1690vs	1615m	1583vs
(VIII)	NMe	OMe	—	1675vs	1613vs	1579m
(IX)	OMe	OMe	—	—	1617w	1592m 1587m

In these Tables bands quoted are for the spectra of mulls; positions are all in cm.$^{-1}$ units. Intensities are designated in the conventional manner. * indicates shoulder.

The 1550—1350 *cm.*$^{-1}$ *Region.*—Absorption hereabouts would be expected from ring stretching modes, *O*- and *N*-methyl CH-deformation modes, and possibly NH-deformation modes. The small number of compounds available does not allow a detailed assignment, but differences are found between the absorption of the three main types of compound (see Table 2).

The 1350—1100 *cm.*$^{-1}$ *Region.*—The ring-oxygen stretching frequency of the methoxy-compound appears as two or more strong bands at 1330—1230 cm.$^{-1}$, which are noticeably absent from the other compounds (see Table 3).

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[4] Katritzky and Jones, *J.*, 1959, 3670.
[5] Katritzky and Jones, *J.*, 1960, 2947.
[6] Katritzky and Coats, *J.*, 1959, 2062.

The 1100—750 *cm.*$^{-1}$ *Region.*—In this region (see Table 4) the spectra show the in- and out-of-plane CH-deformation bands, which should be similar for all the compounds.

Other Compounds.—The spectra of 6-chloro- and 6,7-dichloro-quinoxaline-2,3-dione, the mono-*N*-methyl derivatives of 6-chloro-, 6-nitro-, and 6-bromo-quinoxaline-2,3-dione, and the di-*N*-methyl derivatives of 6-chloro- and 6-bromo-quinoxaline-2,3-dione indicate that all these compounds also exist in the di-oxo-form. The detailed spectra will be submitted to the DMS scheme (Butterworths).

TABLE 2. *The* 1550—1350 *cm.*$^{-1}$ *Region.*

(IV)	1507m	1481m	1427m	1397s
(V)	1522m 1510m	1465 *	1443m	1394s
(VI)	1514m	1481 * 1462m	1427m	1379s
(VII)	1495m	1461m	1450w 1440w	1385w
(VIII)	1495 *	1480m 1460*	1445m	1417w
(IX)	1527m 1503w	1487s 1458m	1426m	1379s

TABLE 3. *The* 1350—1100 *cm.*$^{-1}$ *Region.*

	Ring stretching		OMe	β-CH	OMe	β-CH	NMe and β-CH
(IV)	1335w	1315w	—	1258m	—	—	1125w
(V)	1334w	1312w	—	1261m	—	1159m	1139w 1125m
(VI)	1327 *	1311m	—	1268m	—	1162w	1150w 1102w
(VII)	1341m	—	1309vs	1279w 1267w	1245vs	1157w	1118w
(VIII)	1338m	—	1324s 1305s	1280w	1246vs 1225w	1182w	1160w 1120m
(IX)	—	—	1330s 1320m	1290w 1262w	1248m 1223s	1191m 1175m	1148w

TABLE 4. *The* 1100—750 *cm.*$^{-1}$ *Region.*

	NMe	β-CH	OMe	γ-CH	?	γ-CH	γ-CH
(IV)	—	1033w	—	943w	892w	862m 853m	758m 751m
(V)	1043w	1030w	—	933w	898w	863m	749s
(VI)	1058w	1022w	—	932w	913w	—	749s
(VII)	—	1029w	1005s	946w 933w	903w	880 853w	759m 749s
(VIII)	1049m	1040 *	972m	943w	908w	858w	758vs
(IX)	—	1019m	997s	951m	920w	891m	757s

Experimental.—Preparation of the compounds has been described previously.[3] The spectra were measured on a Perkin–Elmer model 21 instrument for the solutions and Nujol mulls, and on an Infracord for the potassium bromide discs.

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