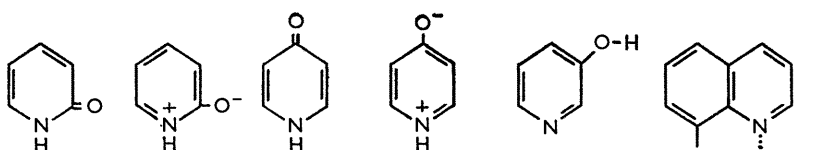
980. *The Tautomerism of N-Heteroaromatic Hydroxy-compounds. Part I. Infrared Spectra.*

By S. F. Mason.

The infrared spectra of a number of *N*-heterocyclic hydroxy-compounds have been measured in the O–H, N–H, and double-bond stretching-vibration regions. The compounds with a hydroxyl group α or γ to a ring-nitrogen atom absorb in the N–H and C:O stretching vibration regions both in the solid state and in chloroform solution, and so possess principally amide structures under these conditions. The remaining compounds have mainly enolic structures in solution, showing absorption due to a free or an intramolecularly hydrogen-bonded O–H group. The infrared evidence for the zwitterionic structure of the latter group of compounds in the solid state is discussed. The compounds which tautomerise to an amide with a quasi-*o*-quinonoid structure (*e.g.*, I) show an N–H stretching vibration absorption in the range 3360—3420 cm.$^{-1}$, whilst their quasi-*p*-quinonoid isomers (*e.g.*, II) absorb in the range 3415—3445 cm.$^{-1}$, and their analogues with five-membered rings (*e.g.*, VIII) in the range 3440—3485 cm.$^{-1}$. The position of the C:O band of such compounds depends upon the structural type and the number of nitrogen atoms in the ring carrying the potentially tautomeric hydroxyl group. For nuclei similarly substituted, the C:O band of the quasi-*o*-quinonoid amides lies at a higher frequency than that of the quasi-*p*-quinonoid isomers. The structures of some dihydroxy- and polyaza-compounds are elucidated by means of these correlations.

It has been shown by infrared spectroscopy that 2- and 4-hydroxy-pyridine,[1,2] -pyrimidine,[3] and -quinazoline,[4] and 2-hydroxyquinoline,[2] exist predominantly as amide forms in the solid state. In the present work an infrared study has been made of a wide range of such *N*-heterocyclic hydroxy-compounds, in the solid state and in chloroform and carbon tetrachloride solution. The results (Table 1) show that in solution all the compounds with a hydroxyl group α or γ to a ring-nitrogen atom absorb in the amide C:O (1630—1780 cm.$^{-1}$) [5] and N–H (3360—3500 cm.$^{-1}$) [5] stretching vibration regions. They exist, therefore, mainly in amide forms (*e.g.*, I or II respectively) in solution. The compounds with a hydroxyl group which is neither α nor γ to a ring-nitrogen atom give rise in solution (Table 2) to a sharp band near to 3600 cm.$^{-1}$, due to a free O–H stretching vibration or, if the hydroxyl group is *peri* to a ring-nitrogen atom, to a broad band in the range 3395—3470 cm.$^{-1}$, due to an intramolecular hydrogen-bonded O–H stretching vibration. The latter bands have widths at half-extinction of 60—100 cm.$^{-1}$ in dilute solution, whilst the compounds with amide structures give N–H bands with half-widths of 15—30 cm.$^{-1}$ under



the same conditions, allowing the two types to be distinguished. The compounds with a hydroxyl group which is neither α nor γ to a nitrogen atom do not absorb in the amide

[1] Sensi and Gallo, *Ann. Chim.* (*Italy*), 1954, **44**, 232.
[2] Gibson, Kynaston, and Lindsey, *J.*, 1955, 4340.
[3] Brown and Short, *J.*, 1953, 331; Brown, Hoerger, and Mason, *J.*, 1955, 211.
[4] Culbertson, Decius, and Christensen, *J. Amer. Chem. Soc.*, 1952, **74**, 4834.
[5] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954; "Chemical Applications of Spectroscopy," ed. W. West, Technique of Organic Chemistry, Vol. IX, Interscience, New York, 1956.

TABLE 1. *The infrared spectra of α- and γ-hydroxy-N-heteroaromatic compounds in the N–H, O–H, and C=O stretching vibration regions. Values in italics refer to carbon tetrachloride solution; the other solution values refer to chloroform as solvent.* (s = *strong* m = *medium*, w = *weak*.)

No.	Compound	N–H stretching frequencies (cm.$^{-1}$) In soln.	In the solid state	C=O stretching frequencies (cm.$^{-1}$) In soln.	In the solid state
	(I) *α-Hydroxy-compounds with six-membered ring systems.*				
1	2-Hydroxypyridine	*3404*, 3398	3198 m, 3165 s	1654	1650 s
2	2-Hydroxypyrazine	*3399*, 3393	3257 m, 3166 s	1730	1710 s, 1662 s
3	3-Hydroxypyridazine	*3394*, 3387	3237 m, 3194 s	1681	1678 s, 1652 s
4	2-Hydroxypyrimidine	*d* 3394	3195 m	1765	1733 m, 1647 s
5	2-Hydroxyquinoline	*3394*, 3386	3280 w, 3252 m	1656	1648 s
6	1-Hydroxy*iso*quinoline	*3418*, 3411	3278 w, 3150 s	1658	1653 s
7	3-Hydroxycinnoline	*3371*, 3367	3288 w, 3220 m	1660	1660 s
8	1-Hydroxyphthalazine	*3408*, 3401	3292 w, 3240 m	1674	1658 s
9	2-Hydroxyquinoxaline	*3391*, 3384	3290 w, 3258 m	1673	1690 m, 1642 s
10	8-Hydroxy-1 : 7-naphthyridine	*d* 3403	3308 w, 3095 s	1665	1693 s
11	5-Hydroxy-1 : 4 : 6-triazanaphthalene	*d* 3401	3330 w, 3145 s	1687	1692 s, 1650 s
12	9-Hydroxyphenanthridine	*3411*, 3402	*e*	1669	*e*
	(II) *α-Hydroxy-compounds with five-membered ring systems.*				
13	2-Hydroxybenziminazole	*3481*, 3469	*e*	1722	1728 s
14	2-Hydroxyimidazo[4 : 5-*b*]pyrazine	*d* 3441	*e*	1752	*e*
15	8-Hydroxy-7-methylpurine [a]	*3456*, 3444	*e*	1739	1742
16	8-Hydroxy-9-methylpurine [a]	*3465*, 3450	*e*	1744	1745
	(III) *γ-Hydroxy-compounds.*				
17	4-Hydroxypyridine	3442	3200 m, 3104 s	1638	1638 s
18	4-Hydroxypyridazine	*3438*, 3430	3288 m, 3078 m	1662	1660 m, 1640 s
19	4-Hydroxyquinoline	*3442*, 3438	3226 m, 3140 m	1645	1638 s
20	4-Hydroxycinnoline	*3427*, 3422	3222 m, 3190 s	1638	1610 s
21	8-Hydroxy-1 : 4 : 5-triazanaphthalene	*d* 3415	3198 w, 3173 m	1631	1625 s
22	5-Hydroxy-4-methylacridine	*3439*, 3434	*e*	1633	*e*
23	4-Hydroxy-2-methylbenzo[*g*]quinoline	*3443*, 3436	*e*	1645	*e*
24	4-Hydroxy-2-methyl-1 : 10-phenanthroline	*3389*, 3374	*e*	1634	*e*
	(IV) *αγ-Dihydroxy- and αγ-diaza-compounds.*				
25	4-Hydroxypyrimidine	*3395*, 3390	3257 m, 3200 s	1721	1716 m, 1684 s
26	2 : 4-Dihydroxy-1-methylpyrimidine	*d* 3395	*e*	1713, 1689	*e*
27	2 : 4-Dihydroxy-3-methylpyrimidine	*d* 3432	*e*	1717, 1661	*e*
28	4-Hydroxyquinazoline	*3402*, 3397	3365 w, 3205 s	1681	1663 s
29	4-Hydroxy-1 : 3 : 5-triazanaphthalene	*d* 3389	3177 m, 3095 s	1746	1710 s, 1670 s
30	6 : 7-Diethyl-4-hydroxypteridine [b]	*3401*, 3387	*e*	1685	*e*
31	6 : 7-Diethyl-2 : 4-dihydroxypteridine	*3421*, 3412 *3408*, 3395	*e*	1719, 1687	*e*
32	6-Hydroxy-7-methylpurine [a]	*d* 3390	*e*	1702	1697
33	6-Hydroxy-9-methylpurine [a]	*d* 3388	*e*	1711	1679
	(V) *Related compounds.*				
34	2-Pyrrolidone [c]	*3505*	3225	*1706*	1690
35	2-Piperidone [c]	*3425*	3236, 3096	*1672*	1669
36	Phthalimide	*3443*, 3431	*e*	1778, 1739	*e*
37	Homophthalimide	*3389*, 3383	*e*	1699	*e*

[a] Quoted from Brown and Mason (*J.*, 1957, 682). [b] Quoted from Brown and Mason (*J.*, 1956, 3443). [c] Quoted from Mecke and Mecke (*Chem. Ber.*, 1956, **89**, 343). [d] Insufficiently soluble. [e] Not measured.

C:O range (Table 4). Accordingly, these compounds possess enolic structures (*e.g.*, III and IV) in solution, even where tautomerism to vinylogous amide forms is possible (*e.g.*, V; R = H).

In the solid state the compounds with a hydroxy-group α or γ to a ring-nitrogen atom

give rise to an amide C:O band, which in general, but not invariably, is at a lower frequency than in solution (Table 1). Saturated cyclic and open-chain amides [5] show a similar lowering, which has been ascribed to hydrogen-bonding [6] or to dipole–dipole interaction [7] in the solid state. The fact that, in some cases, the C:O frequency is greater in solution than in the solid state favours the hypothesis of dipole–dipole interaction, as

TABLE 2. *The infrared spectra of enolic* N-*heterocyclic hydroxy-compounds in the* O–H *and double-bond stretching vibration regions.* (s = *strong*, m = *medium*, w = *weak*, b = *broad*.)

No.	Compound	O–H stretching frequencies ($cm.^{-1}$) In CCl_4 soln.	O–H stretching frequencies ($cm.^{-1}$) In the solid state	Double-bond stretching frequencies in the solid state ($cm.^{-1}$)
38	3-Hydroxypyridine	3595	2925—2500 m + b	1573 s, 1476 s
39	3-Hydroxyquinoline	3591	2942—2525 m + b	1598 s, 1469 s
40	5-Hydroxyquinoline	3599	2945—2550 m + b	1616 m, 1580 s
41	6-Hydroxyquinoline	3601	2960—2500 m + b	1633 w, 1577 s
42	7-Hydroxyquinoline	3597	2960—2525 m + b	1615 s, 1533 s
43	8-Hydroxyquinoline	3412 b	3180 s + vb	1577 s, 1507 s
44	4-Hydroxy*iso*quinoline	3603	2900—2500 m + b	1626 m, 1582 s
45	5-Hydroxy*iso*quinoline	3615	2950—2550 m + b	1623 m, 1588 s
46	6-Hydroxy*iso*quinoline	3610	2920—2620 m + b	1625 m, 1614 s
47	7-Hydroxy*iso*quinoline	3619	2900—2600 m + b	1628 m, 1589 s
48	8-Hydroxy*iso*quinoline	3611	2920—2550 m + b	1621 m, 1557 s
49	8-Hydroxycinnoline	3440 b	3100 s + vb	1624 m, 1582 m
50	6-Hydroxyquinazoline	3603	3125 s, 2933—2600 m + b	1640 m, 1582 s
51	8-Hydroxyquinazoline	3440 b	3145 s + vb	1624 m, 1592 s
52	5-Hydroxyquinoxaline	3470 b	3418 m, 3322 s, 3225 m	1625 m, 1583 s
53	6-Hydroxyquinoxaline	3596	2950—2500 m + b	1618 s, 1522 s
54	8-Hydroxy-1 : 6-naphthyridine	3456 b	3314 m, 3245 s, 3125 s	1614 m, 1578 m
55	2-Hydroxyphenanthridine	3617	2922—2532 m + b	1614 s, 1574 m
56	6-Hydroxyphenanthridine	3607	2892—2590 m + b	1628 m, 1605 s
57	7-Hydroxyphenanthridine	3613	2923—2549 m + b	1627 m, 1574 s
58	1-Hydroxyacridine	3398 b	*a*	*a*
59	3-Hydroxyacridine	3611	*a*	*a*
60	4-Hydroxyacridine	3607	*a*	*a*
61	1-Hydroxyphenazine	3448 b	*a*	*a*
62	2-Hydroxyphenazine	3602	*a*	*a*
63	6-Hydroxy-1 : 7-phenanthroline	3395 b	*a*	*a*

[a] Not measured.

TABLE 3. *The infrared spectra, in the solid state, of some* N-*heteroaromatic hydroxy-compounds insoluble in chloroform, in the* N–H, O–H, *and double-bond stretching vibration regions.* (s = *strong*, m = *medium*, w = *weak*, b = *broad*.)

No.	Compound	N–H or O–H stretching frequencies ($cm.^{-1}$)	Double-bond stretching frequencies ($cm.^{-1}$)
64	2 : 4-Dihydroxypyridine	3230 w, 2915—2520 m + b	1661 s, 1635
65	5-Hydroxypyrimidine	2922—2532 m + b	1608 s, 1568 s
66	2 : 4-Dihydroxyquinoline	3250 w, 2908—2525 m + b	1662 s, 1628 s
67	4 : 8-Dihydroxyquinoline	3340 s, 2880—2530 m + b	1621 s, 1570 s
68	5-Hydroxycinnoline	2921—2555 m + b	1621 m, 1579 s
69	6-Hydroxycinnoline	3145 w, 2875—2600 m + b	1640 m, 1590 s
70	7-Hydroxycinnoline	2915—2620 m + b	1622 s, 1565 s
71	6-Hydroxyphthalazine	3372 m, 3264 s	1649 m, 1618 s
72	2-Hydroxyquinazoline	3313 w, 3194 s	1680 s, 1608 s
73	4-Hydroxy-1 : 5-naphthyridine	3203 w, 3108 m	1624 s, 1586 m

the C:O frequency could be increased by hydrogen-bonding only if the C:O···H angle were $<90°$, a configuration which is unfavourable for hydrogen-bonding. In most of the cases (compounds 9, 10, 11, 15, 16) N–H···N hydrogen-bonding might allow weak ancillary N–H···O hydrogen-bonding with a C:O···H angle $<90°$ (*e.g.*, VI), but such bonding would not be possible in the case of 2-hydroxybenziminazole (VIII).

[6] Krimm, *J. Chem. Phys.*, 1955, **23**, 1371.
[7] Cannon, *Mikrochim. Acta*, 1955, 555; *J. Chem. Phys.*, 1956, **24**, 491.

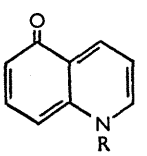
The N–H and O–H bands of *N*-heterocyclic hydroxy-compounds in the solid state fall into three general classes (Table 1, 2, and 3). The α- and γ-hydroxy-compounds absorb mainly in the range 3100—3300 cm.$^{-1}$, the bands being sharp, whilst the *peri*-compounds give very broad bands in the same region, and the remainder show broad bands between 2450 and 2950 cm.$^{-1}$. Empirical correlations have been established between the X–H···Y distance (R) of intermolecular hydrogen-bonds and the frequency shift ($\Delta\nu$) of the X–H stretching vibration absorption.[8,9] O–H···O absorptions fall off rapidly with decreasing distance according to the relation: [8]

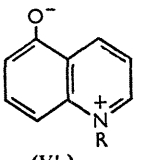
$$\Delta\nu = 4{\cdot}43 \times 10^3(2{\cdot}84 - R)$$

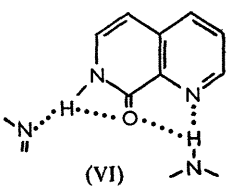
whilst N–H···O absorptions fall off more slowly, following the relation: [8]

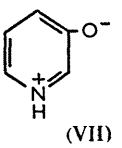
$$\Delta\nu = 0{\cdot}548 \times 10^3(3{\cdot}21 - R)$$

It is probable, therefore, that α- and γ-hydroxy-compounds are N–H···O hydrogen-bonded with distances of 2·6—3·0 Å between the bonded centres, whilst the remainder, apart from the *peri*-hydroxy-compounds, are O–H···O hydrogen-bonded with distances of 2·56—2·72 Å between the bonded centres. Some polyaza-members of the latter group absorb above 3100 cm.$^{-1}$ (compounds 50, 69, and 71, Tables 2 and 3) and may be also O–H···N hydrogen-bonded, as this bond absorbs at frequencies which fall slowly with decreasing bond distance.[9] The *peri*-hydroxy-compounds may remain intramolecularly O–H···N hydrogen-bonded in the solid state, as they absorb in the range 3100—3200 cm.$^{-1}$ expected [9] for the calculated oxygen–nitrogen distance of 2·7 Å. However, intramolecular O–H···O bonds do not follow the frequency–bond distance relation established for intermolecular bonds.[9]


(Va)


(Vb)


(VI)


(VII)

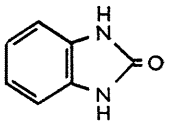
A zwitterion structure for 3-hydroxypyridine (VII) in the solid state has been proposed,[1] as it absorbs in the hydrogen-bonded $^+$N–H stretching vibration region of the amino-acids near 2000 cm.$^{-1}$. This is not good evidence for the structure (VII), since the nitrogen atom in the amino-acid zwitterions is in a sp^3 state of hybridisation, whilst in (VII), as in (I) and (V), it is in a sp^2 state. For quadricovalent nitrogen in a sp^3 state, the free N–H stretching frequency [9] is near 3100 cm.$^{-1}$, and the hydrogen-bonded frequencies [8] cover a range down to 2000 cm.$^{-1}$, whilst the corresponding frequencies for quadricovalent nitrogen in a sp^2 state may be expected to be close to those recorded in Table 1 for the compounds with amide structures. However, the *N*-heteroaromatic hydroxy-compounds in which the nitrogen and the oxygen atoms are not conjugated exist partly as zwitterions in aqueous solution,[10] and possibly also in the solid state. In the double-bond stretching vibration region the spectra of the hydroxyquinolines in the solid state, but not in solution, resemble those of the corresponding *N*-methyl derivatives with fixed zwitterionic structures (Tables 2 and 4). The bands observed are due to ring stretching modes which should be sensitive to structural changes, such as the tautomerism from enol to zwitterion, but 5- and 7-hydroxyquinoline do not absorb in the amide C:O region whilst their *N*-methyl derivatives, to the structure of which vinylogous amide forms contribute (*e.g.*, Va, R = Me), absorb in the C:O range (Tables 2 and 4).

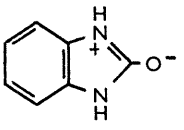
[8] Pimentel and Sederholm, *Mikrochim Acta*, 1955, 639.
[9] Nakamoto, Margoshes, and Rundle, *J. Phys. Chem.*, 1955, **77**, 6480.
[10] Part II, following paper.

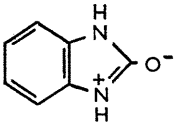
TABLE 4. *The infrared spectra, in chloroform solution, of the enolic hydroxyquinolines and their* N*-methyl derivatives (zwitterionic forms) in the double-bond stretching vibration region.*

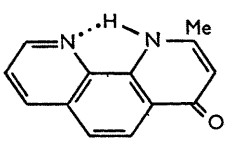
No.	Compound	Frequencies ($cm.^{-1}$)	No.	Compound	Frequencies ($cm.^{-1}$)
39	3-Hydroxyquinoline	1614	42	7-Hydroxyquinoline	1621
74	1-Methyl- ,, ...	1592	77	1-Methyl- ,, ...	1639, 1598
40	5-Hydroxyquinoline	1619	43	8-Hydroxyquinoline	1628
75	1-Methyl- ,, ...	1648, 1573	78	1-Methyl ,, ...	1573
41	6-Hydroxyquinoline	1616			
76	1-Methyl- ,, ...	1583			

In solution the N–H bands of *N*-heteroaromatic hydroxy-compounds which tautomerise predominantly to amide forms fall into ranges, depending upon the structural type. The quasi-*o*-quinonoid amides (*e.g.*, I) absorb between 3360 and 3420 $cm.^{-1}$, whilst their quasi-*p*-quinonoid isomers (*e.g.*, II) absorb between 3415 and 3445 $cm.^{-1}$ and their analogues with five-membered rings (*e.g.*, VIII) between 3440 and 3485 $cm.^{-1}$ (Table 1). Aza-substitution in any of the three structural types lowers the N–H stretching frequency, so that there is some overlap of the ranges, but the mono- and di-aza-members of each type absorb over more restricted and distinct regions (Table 1). An exception is 4-hydroxy-2-methyl-1 : 10-phenanthroline which absorbs at a lower frequency than the other diaza-members of the quasi-*p*-quinonoid type (Table 1), owing to intramolecular hydrogen-banding (IX). The N–H band of this compound has a width at half-extinction of 25 $cm.^{-1}$, and so it cannot be distinguished from the free N–H absorption of the quasi-*o*-quinonoid amides by its width (see above).


(VIIIa)


(VIIIb)


(VIIIc)

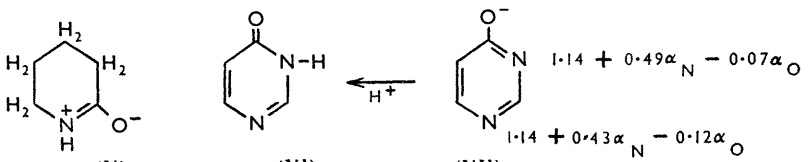

(IX)

The position of the C:O band of the compounds which tautomerise predominantly to amide forms is more sensitive than that of the N–H band to aza-substitution, particularly to substitution in the ring carrying the tautomeric hydroxyl group. The quasi-*o*-quinonoid amides with not more than one nitrogen atom in the ring substituted by the hydroxyl group give a C:O band in the range 1654—1687 $cm.^{-1}$, whilst the corresponding quasi-*p*-quinonoid amides absorb between 1630 and 1645 $cm.^{-1}$ in solution (Table 1). The high frequency of the C:O band and the low frequency of the N–H band of the quasi-*o*-quinonoid amides, relative to their quasi-*p*-quinonoid isomers, may be ascribed to an inducto-electromeric effect between the atoms of the amide group. The nitrogen atom enhances the electronegativity of the carbon atom of the C:O group, and so increases the double-bond character of that group, whilst the nitrogen atom becomes positively charged by the inductive effect of the oxygen atom. In general, the stretching frequency of the N–H group falls as the nitrogen atom becomes more positively charged, indole,[11] for example, absorbing at 3484 $cm.^{-1}$ and purine [12] at 3441 $cm.^{-1}$ in chloroform solution. In the three structural types of amide, positive charge on the N–H group arises also by resonance (*e.g.*, between Ia and b; IIa and b; VIIIa, b, and c). The charge is localised in the six-membered ring compounds, but it is shared with another N–H group in the five-membered ring amides, and the stretching frequency of the N–H group is higher in the latter compounds than in the former. Ring strain may also contribute, as the frequency of the N–H absorption is higher in 2-pyrrolidone than in 2-piperidone (Table 1). In both the N–H and C:O regions 2-piperidone absorbs at higher frequencies than its aromatic analogue, 2-hydroxypyridine (Table 1), indicating that the zwitterion resonance form (Ib), in which the aromatic

[11] Mason, unpublished results.
[12] Brown and Mason, *J.*, 1957, 682.

resonance is preserved, contributes more to the structure of the latter than the corresponding form (X) to the structure of the former.

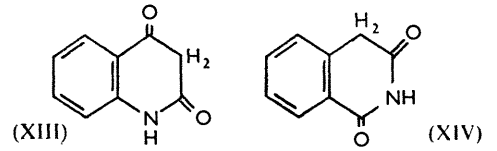
The correlations established above may be used to determine the structure of *N*-heterocyclic hydroxy-compounds which may tautomerise to more than one amide form.[12,13] In the cases of 4-hydroxy-pyrimidine, -quinazoline, -1 : 3 : 5-triazanaphthalene, and -pteridine, and 6-hydroxy-7-, and -9-methylpurine, a tautomeric hydroxyl group is placed both α and γ to a ring-nitrogen atom, and they may form either quasi-*o*- or quasi-*p*-quinonoid amides. The N–H band of these compounds lies in the range characteristic of the quasi-*o*-quinonoid amides (Table 1), and thus they have the structure of that type (*e.g.*, XI). This conclusion is supported by ultraviolet spectroscopy for the cases of 4-hydroxy-pyrimidine,[3] -quinazoline,[14] and -pteridine,[13] though it is surprising in view of the classical generalisation that *p*-quinonoid structures are more stable than isomeric *o*-quinonoid structures. However, the molecular-orbital theory indicates that, granted certain assumptions, the structure of 4-hydroxypyrimidine should be (XI). Considered as a perturbed benzyl anion, the anion of 4-hydroxypyrimidine has the charge distribution (XII), where α_N and



(X) (XI) (XII)

α_O are the differences between the Coulomb integrals of the nitrogen and oxygen atoms respectively and the Coulomb integral of carbon, in terms of the C:C resonance integral, β. A proton will bond to the nitrogen atom with the higher charge density in the anion of 4-hydroxypyrimidine, namely to the 3-, rather than to the 1-nitrogen atom, if α_N is positive and α_O has a positive or small negative value. These conditions are reasonable in view of the relative electronegativities of carbon, nitrogen, and oxygen.[15]

2 : 4-Dihydroxy-pyridine and -quinoline, with hydroxyl groups both α and γ to a ring nitrogen atom, may tautomerise to quasi-*o*- or -*p*-quinonoid amides, or to keto-amides (*e.g.*, XIII). These compounds are insufficiently soluble in chloroform to give infrared spectra in solution, but in the solid state they give two bands in the double-bond region, one in the range of the monoaza-*o*-quinonoid amides, and the other in, or near to, the range for the quasi-*p*-quinonoid isomers (Table 3). It is probable, therefore, that in the solid state both quasi-*o*- and -*p*-quinonoid amide forms occur in these compounds. The ultraviolet evidence indicates that for 2 : 4-dihydroxypyridine the quasi-*o*-quinonoid amide form predominates in aqueous solution.[16] Tautomerism to the keto-amide does not occur, as (XIII) should absorb [5] between 1680 and 1700 cm.$^{-1}$. Homophthalimide absorbs in this range, but not in the O–H stretching vibration region in solution (Table 1), and therefore possesses the analogous structure (XIV). 4 : 8-Dihydroxyquinoline in the



(XIII) (XIV)

solid state does not absorb strongly in the double-bond region above 1621 cm.$^{-1}$ (Table 3), a frequency rather low for an amide C:O vibration, and near to a ring-stretching vibration in quinoline itself [11] at 1620 cm.$^{-1}$. Tautomerism to the amide form may be suppressed in

[13] Brown and Mason, *J.*, 1956, 3443.
[14] Hearn, Morton, and Simpson, *J.*, 1951, 3318.
[15] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[16] Den Hertog and Buurman, *Rec. Trav. chim.*, 1956, **75**, 257.

this case by intramolecular hydrogen-bonding between the 8-hydroxy-group and the ring-nitrogen atom.

Experimental

Infrared Spectra.—These were measured with a Perkin-Elmer model 12C spectrometer with a lithium fluoride prisms for the O–H and N–H stretching vibration regions and a sodium chloride prism for the double-bond stretching vibration region. The compounds were examined at concentrations of 10^{-2} to 10^{-3}M in cells of 5 cm. (CCl_4) or 1 cm. ($CHCl_3$) thickness in the O–H and N–H regions, and 1 mm. in the double-bond region, and as solids included in pressed potassium bromide discs. Band half-widths were measured at a constant slit width of 0·05 mm.

Molecular-orbital Calculation.—The list of atom–atom polarisabilities of the benzyl anion recorded by Jaffé [17] was used in calculations of the charge distribution in the anion of 4-hydroxypyrimidine. The 4 : 4 and 4 : 4′ polarisabilities in this list are incorrect in sign.

Materials.—5-, 6-, and 7-Hydroxycinnoline and 6-hydroxyphthalazine were kindly supplied by Dr. K. Schofield.[18] Homophthalimide, 1-hydroxyphthalazine, and 4-hydroxy*iso*quinoline by Professor N. B. Chapman, 5-hydroxypyrimidine by Dr. J. F. W. McOmie, 5-, 6-, 7-, and 8-hydroxy*iso*quinoline by Dr. R. A. Robinson,[19] 2-, 6-, and 7-hydroxyphenanthridine by Dr. M. M. Coombs, [20] 3- and 4-hydroxypyridazine by Dr. J. Druey, and 2-hydroxyimidazo-[4 : 5-*b*]pyrazine by Dr. H. T. Openshaw. The remaining compounds were kindly provided by Professor A. Albert.[21]

The author thanks Professor A. Albert for helpful discussion, Mr. D. Light for technical assistance, and the Australian National University for a Research Fellowship, during the tenure of which the present work was carried out.

Australian National University.
[Present address: The University, Exeter.]

[*Received, June 6th,* 1957.]

[17] Jaffé, *J. Amer. Chem. Soc.*, 1954, **76**, 3527.
[18] Osborn and Schofield, *J.*, 1956, 4207.
[19] Robinson, *J. Amer. Chem. Soc.*, 1947, **69**, 1939, 1942, 1944.
[20] Arcus and Coombs, *J.*, 1954, 4319.
[21] Albert and Phillips, *J.*, 1956, 1294.