The Electronic Structure of Groups of Isomeric Hetero-Aromatic Systems

III. Hydroxy-Pyridines and Pyridones

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A discussion of the electronic structure of hydroxy-pyridines and pyridones shows that there is no reason for the point of view that the 3-oxo isomer, β-pyridone, does not exist. N-methyl-3-pyridone was prepared and characterized to check this conclusion.

The incorrect view is due to the assumption that the electron pairing scheme adopted in the valence bond method is necessarily implied in the classical formulae. This assumption should be replaced by a valence state interpretation of the classical symbols of atoms in molecules, independently of the method chosen for constructing the molecular wave-function.

Eine Diskussion der Elektronenstruktur von Hydroxy-Pyridinen und Pyridonen zeigt, daß es keinen Grund für die Annahme gibt, daß das 3-Oxo isomere β-Pyridon nicht existiert. N-Methyl-3-Pyridon wurde hergestellt und untersucht, um diesen Schluß zu prüfen. Der unkorrekte Standpunkt rührt von der Annahme her, daß das Elektronenpaar, welches der Valenzstrukturmethode zugrunde liegt, notwendigerweise in der klassischen Formel enthalten ist. Diese Annahme sollte durch eine Interpretation des Valenzzustandes der klassischen Symbole von Atomen in Molekülen ersetzt werden, unabhängig von der Methode, die zur Konstruktion der Molekülwellenfunktion gewählt wird.

La discussion de la structure électronique des hydroxy-pyridines et des pyridones a montré qu'il n'y a pas lieu de supposer que l'isomère 3-oxo, ou β-pyridone, n'existe pas. Cette conclusion a été confirmée par l'obtention et la caractérisation du N-methyl-3-pyridone.

On a trouvé que cette opinion incorrecte est due à l'hypothèse suivante: le schéme de couplage électronique utilisé dans la méthode de la mesomerie (méthode V.B.) doit être appliqué aux formules classiques. Cette hypothèse n'est pas necessaire et devrait être remplacée par une interprétation des symboles classiques des atomes dans les molécules en fonction des états de valence atomiques, indépendamment de la méthode choisie pour la construction de la fonction d'onde moléculaire.

Introduction

Pyridones, the lactam- or amide-like tautomers of hydroxy-pyridines, are a particular case of the conjugated systems characterized by a group eight π-electrons, seven of which belong to a planar cyclic structure and one to an extra-cyclic atom or group.

Two of the three possible isomers, α- and γ-pyridones, and their N-substituted derivatives, have long been known and extensively studied. The literature on β-pyridones, on the other hand, shows a certain degree of confusion, as can be seen from the following selection of quotations: "3-Hydroxy-pyridine ... cannot exist in a pyridone form" [1]; "A corresponding *(pyridone)* structure is not possible

for 3-hydroxy-pyridine" [2]; "3-Hydroxy-pyridine ... from considerations of valency cannot assume an amide form" [3]; "With β-hydroxy-pyridine, on the other hand, the tautomerism is of the keto-enol" [4] (to distinguish it from the lactam-lactim type tautomerism of the α- and γ-derivatives). Other authors consider that 3-hydroxy-pyridine-methochloride, dissolved under appropriate conditions, can give origin to a dipolar ion, or zwitter-ion I [5–7]. Finally, even the name "β-pyridone" does not seem to have reappeared in the literature since 1945, when Tchitchibabine [8] used it in his last paper.

Me   I
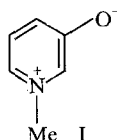
This state of affairs goes back to the controversy on the symbols $-N\lessgtr$ and $-N\lessdot$, as they were used, for example in the nitro group or in pyrrol respectively. As we have shown previously [9], they identify the same valence state of nitrogen, $N(tr\,tr\,tr\,\pi^2, V_3)$, and are completely equivalent in any molecule where nitrogen bound to three neighbouring atoms has a planar coordination. This equivalence was not recognized in classical chemistry. For example Ibele in his thesis (Munich, 1905) [10] represented with the formula II the red compound he had synthesized from quinaldinic acid, but this formula was not given in the papers which were published by Besthorn and Ibele [11].

II

III
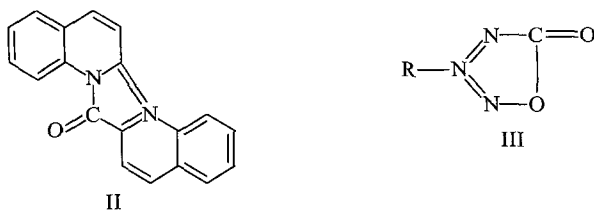
This probably happened because the pentavalency of nitrogen had been objected to as unsatisfactory in a discussion of the structure of the tautomers of the hydroxy-pyridines [12] on the ground of negative evidence for the existence of β-pyridone. The controversy, however, continued and formula III was assigned in 1933 to a series of oxytriazol-5-ones which had been prepared in 1915 [13]. A more recent case is that of the so-called "mesoionics", a name adopted to classify those peculiar compounds for which "...no possible covalent bond structure can be drawn to represent the electronic pairings" [14]. The Besthorn red II and the oxatriazolones III were recognized [15, 16] as examples of this class, and we propose here to add β-pyridone and its derivatives, if their existence is proved possible.

We have therefore carried out a comparative study of the electronic structure of all the tautomeric isomers of the hydroxy-pyridines, and have found no ground for regarding β-pyridones as anomalous in any respect. In order to check this theoretical prediction we also carried out some experiments also reported here, which lead to the same conclusion.

Theory

The first aim of our calculations was to see if any special characteristics could be found in the ground state calculated properties which would differentiate β-pyridone from its α and γ isomers. The method is the same as described in part I of this series [17], and the details relevant to the present case are given in the appendix. The total π-energies, the eigenvalues corresponding to the occupied MO's and the π-dipole moments are listed in Table 1 and the charge diagrams are shown in Fig. 1.

Table 1. *Calculated energies and dipole moments*

	Hydroxy-pyridines			Pyridones		
	2	3	4	α	β	γ
ε_1	$-$ 18.41	$-$ 18.34	$-$ 18.54	$-$ 19.50	$-$ 20.13	$-$ 19.36
ε_2	$-$ 14.89	$-$ 15.10	$-$ 15.10	$-$ 14.33	$-$ 14.49	$-$ 14.49
ε_3	$-$ 12.25	$-$ 12.16	$-$ 11.55	$-$ 14.13	$-$ 13.77	$-$ 13.49
ε_4	$-$ 10.92	$-$ 10.84	$-$ 11.44	$-$ 10.66	$-$ 9.87	$-$ 10.46
E_π	$-$296.82	$-$295.94	$-$295.22	$-$301.91	$-$299.00	$-$299.01
ΔE_π	$-$177.48	$-$176.60	$-$175.88	$-$187.73	$-$184.82	$-$184.83
μ_π	1.68	2.59	3.26	7.07	10.27	10.85
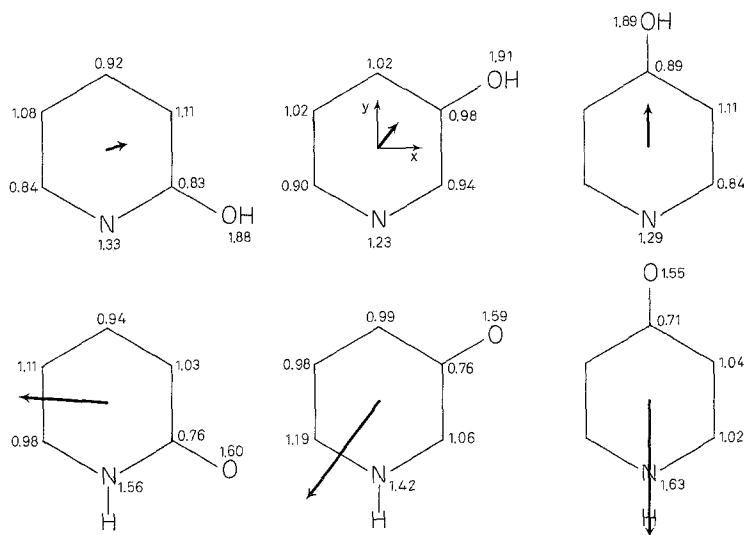
Fig. 1. π-electron distribution and μ_π dipole moment for hydroxy-pyridines and pyridones

The energy data can be commented in several ways. First the total π-energy of the three pyridone isomers is similar, that of the β and γ isomers being about 3 eV, or 1 %, higher than that of the α isomer. The situation is nearly the same with the hydroxy-pyridine tautomeric isomers. To establish a significant relationship between the different tautomers we need to compare the corresponding π-energy

gain with respect to the free atoms in the appropriate valence state:

$$\Delta E_\pi = E_\pi - \sum_k W_k - (2W_p - \gamma_{pp}) \tag{1}$$

with k running over the valence state ionization potentials of the atoms contributing one π-electron to the core, and p referring to the atom contributing two π-electrons.

From these ΔE_π, also given in Table 1, we see that the oxo-tautomer obtains in all cases a larger π-energy gain, and therefore we should expect it to be the more stable electronic structure. The pyridone form should therefore always prevail, unless the potential barrier for displacing the proton from oxygen to nitrogen prevents this from happening. It should be added, however, that the energy gain of the oxo structure with respect to the hydroxy-tautomer is predicted to be the lowest for β-pyridone, although its value, 8.22 eV against 10.25 and 8.95 for α and γ, is not such as to make the prediction doubtful on any comparative ground.

The calculated π-dipole moments again do not suggest any peculiar characteristic for β-pyridone, which again is predicted to be similar to its γ isomer. The charge distribution diagrams only show that its nitrogen orbital π-electron population is 10–15% lower than with the other two isomers, and therefore its positive charge 20–30% higher.

From a theoretical view-point, therefore, one should expect the ground state properties of β-pyridone to be in line with those of its isomers. In particular β-pyridone should be present in a tautomeric equilibrium with its ions and with the hydroxy compound, and it should be possible to obtain it in the form of N-substituted derivatives.

Experimental Results and Discussion

The tautomeric equilibria of aqueous solutions of 3-hydroxy-pyridine as a function of pH have been extensively studied [5, 7] and interpreted in terms of the neutral and ionic species IV, V, VI, and of the zwitter-ion structure I. This latter is taken as the equivalent of the neutral pyridone, but distinct from it as considered
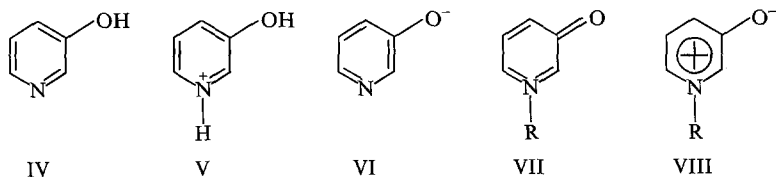
for the α and γ isomers [18]. A different interpretation of these data in terms of a neutral species, to be written as VII or VIII according to the conventions of classical chemistry or of the mesoionic classification [15, 16], although it might appear reasonable in view of our theoretical results, would be meaningless. It is in fact necessary to isolate first these compounds and then to demonstrate their structure, properties and behaviour in solution under comparable conditions.

We have therefore chosen, as a first step, to isolate and to characterize the simplest derivative N-methyl-3-pyridone (VII or VIII, R = Me). We shall re-

port here the principal experimental results which show our theoretical predictions to be correct. A more detailed description and a comparison of the properties of the three pyridones, their N-methyl-derivatives and other related compounds will be published elsewhere.

N-methyl-3-pyridone can be obtained in several ways. It is formed in the reaction of 3-hydroxy-pyridine with diazomethane, in the reaction of N-methyl-3-hydroxy-pyridinium chloride with anhydrons sodium carbonate, and in the thermal decomposition of 3-methoxy-pyridine iodomethylate. Preparation from the dimer of N-methyl-3-hydroxy-pyridinium iodide, a complex salt described by Mecklenborg and Orchin [19] was found to be the most convenient. Details and an analysis are given in the Appendix. The product is a yellow oil, hygroscopic, very soluble in water, moderately soluble in acetone and methylcyanide, nearly insoluble in benzene, chloroform, carbon tetrachloride.

We will first discuss the infrared spectra in the $1300-1700 \text{ cm}^{-1}$ region, shown in Fig. 2, and the measured bands listed in Table 2. The addition of water to N-methyl-3-pyridone in increasing amounts, from $\cong 0.5$ to $\cong 2.5$ moles per mole, caused a progressive decrease in the intensity of the 1590 cm^{-1} band and the appearance of a second band near 1500 cm^{-1}. When the amount of water was increased to obtain an aqueous solution (nearly equal volumes of product and D_2O) the intensity of the 1590 cm^{-1} band was greatly reduced and the 1512 cm^{-1} was replaced by the new band at 1498 cm^{-1}. The same changes occurred in the absorption spectrum when D_2O was added to the acetone solution. They were therefore regarded as evidence for the assignment of the 1590 and 1512 cm^{-1} bands to modes involving the $C=O$ stretching vibration. This is consistent with the assignments made by Coburn and Dudek for the corresponding bands of N-methyl-2-pyridone [20] and of N-methyl-4-pyridone [21], based on the ^{18}O isotopic band shift, as shown in Table 3.

The absorption spectrum of 3-hydroxy-pyridine iodomethylate in D_2O after addition of a great excess of KOH was very similar to that of the liquid film of N-methyl-3-pyridone containing very small amounts of water and discussed above.

In general the IR spectra showed that two different species were present in the concentrate aqueous solution, the free basis, or true neutral pyridone, and some ionic species, most likely its cation.

The proton magnetic resonance spectra were used for examining the resonance peak of the methyl group bound to nitrogen under different conditions. The peak was found at 3.50 p.p.m. in hexadeutero-acetone, at 4.09 p.p.m. in D_2O and $D_2O + KOH$. The fact that only one peak was observed in the aqueous solutions does not contradict the conclusion drawn from the infrared spectra that the neutral molecule and its cation are present in $D_2O + KOH$. The single peak should be the time average between two rapidly exchanging structures,
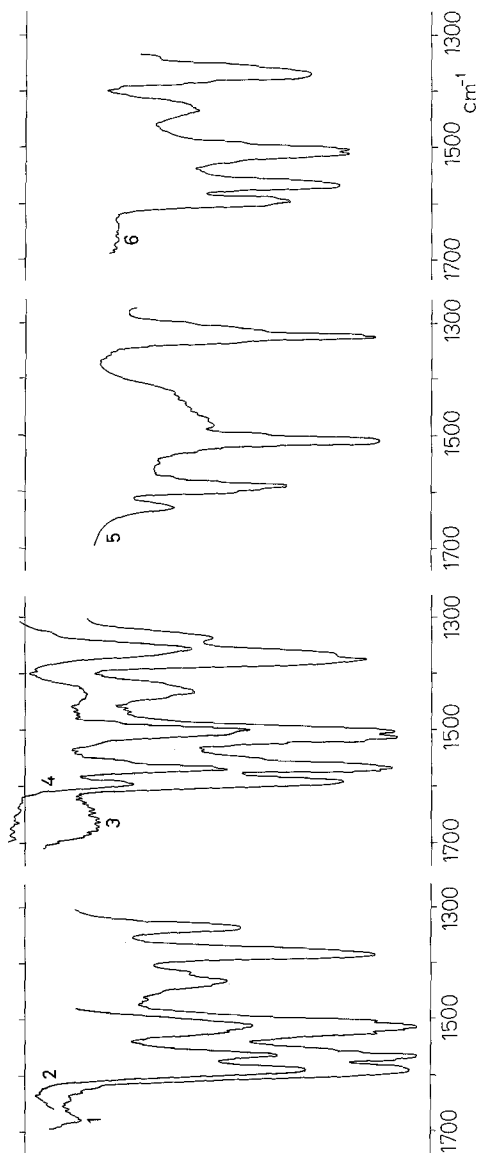

VII   IX
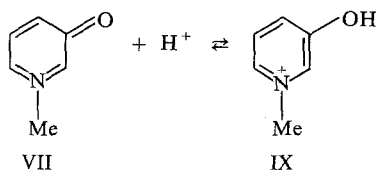
Fig. 2. IR spectra in the 1300–1700 cm^{-1} region. N-methyl-3-pyridone: 1,liquid film; 2,acetone solution; 3, liquid film of the product containing $\cong$ 0.5 moles H$_2$O per mole; 4,D$_2$O solution. 3-Hydroxy-pyridine-iodomethylate: 5,D$_2$O solution; 6,D$_2$O + KOH solution

Table 2. *Measured IR bands in the 1300–1700 cm^{-1} region*

N-methyl-3-pyridone			3-hydroxy-pyridine – Me I	
Liquid film	Acetone sol.	D$_2$O sol.	D$_2$O sol.	D$_2$O + KOH sol.
1590 *vs*	1588 *vs*	1595 *vs*	1630 *m*	
1565 *vs*	1563 *s*	1570 *s*	1592 *s*	1595 *s*
1512 *vs*	1510 *s*	1498 *vs*		1568 *vs*
1432 *m*		1435 *w*	1510 *vs*	1512 *vs*
1382 *s*		1354 *s*	~ 1480 *br, sh*	1503 *vs*
1335 *m*				1432 *m*
			1324 *vs*	1368 *s*

probably not resolved at room temperature by the low frequency of the p.m.r. measurements. The existence of an equilibrium is also supported by the *pH* dependence of the resonance peak, which shifted at 4.34 p.p.m. in $D_2O + DCl$ solution. An identical behaviour was observed with 3-hydroxy-pyridine iodo-methylate: its methyl group showed at 3.98 p.p.m. in hexadeutero-acetone, and at 4.18 p.p.m. in D_2O. After addition of KOH this peak moved to 4.09, and after addition of DCl to 4.34 p.p.m., thus proving that the same species are present in the aqueous solutions of N-methyl-3-pyridone and of the Me I salt of 3-hydroxy-pyridine at the same *pH*.

Table 3. *Carbonyl group stretching modes of N-methyl-pyridones, cm^{-1}*

	2-one[a]	3-one	4-one[a]
v_a	1659	1590	1575
v_b	1583	1512	1401
Δv	76	78	174

[a] Based on the band shift of ^{18}O-labelled compounds (Ref. [20] and [21])

As a test of comparative behaviour we have recorded, under identical conditions, the p.m.r. spectra of N-methyl-2-pyridone. Its methyl peak was found at 2.93 p.p.m. in hexadeutero-acetone, at 3.29 in D_2O and in $D_2O + KOH$, at 4.01 in $D_2O + DCl$. The total shift from the neutral molecule in acetone to its cation in hydrochloric acid was 1.08 p.p.m., compared with 0.84 p.p.m. for the corresponding 3-oxo compound. In order to approximately evaluate the shift due exclusively to solvent change from acetone to water we have recorded the methyl resonance of 3-methoxy-pyridine in hexadeutero-acetone and D_2O, 3.30 and 3.43 p.p.m., respectively. Therefore, assuming the acetone to water shift to be 0.13 p.p.m., the differences $(1.08-0.13) = 0.95$, and $(0.84-0.13) = 0.71$ p.p.m. can be regarded as the respective shifts of the methyl group resonance when the neutral molecules of α- and β-pyridone dissolved in water, were transformed into cations. Let us now take the limiting position of the $\overset{+}{N}$–Me resonance peak of these two cations as the common reference point. The relative shifts 0.95 and 0.71 can be considered to be evidence that the positive charge on the $2p\pi$ orbital of nitrogen in the neutral molecule of β-pyridone is larger than with α-pyridone. This is in agreement with our calculations, which give $+0.58$ versus $+0.44$. It is surprising (even if one does not attach any special significance to the fact) that this qualitative interpretation also enables a quantitative empirical extention to be made, because the calculated charge are inversely proportional to the observed relative shifts as defined above: $0.95 \times 0.44 \cong 0.71 \times 0.58$.

Conclusions

We believe to have shown that the product we have isolated is N-methyl-3-pyridone. The existence of this compound had been denied [1–4], or accepted as possible in aqueous solution in the form of a zwitter-ion. We believe that the

substance we have obtained does not show, *by itself*, a "salt-like character" [7], at least not more so than do its α and γ isomers, which have a structure entirely comparable in the C = O group as shown by the IR absorption spectra, and in the N–Me group as shown by the p.m.r. spectra.

The idea that 3-hydroxy-pyridine can exist only in phenolic form seems to us to be based on presuppositions [1–4] which we have shown not to hold with N-methyl-3-pyridone. To further check on this point we have recorded the IR spectra
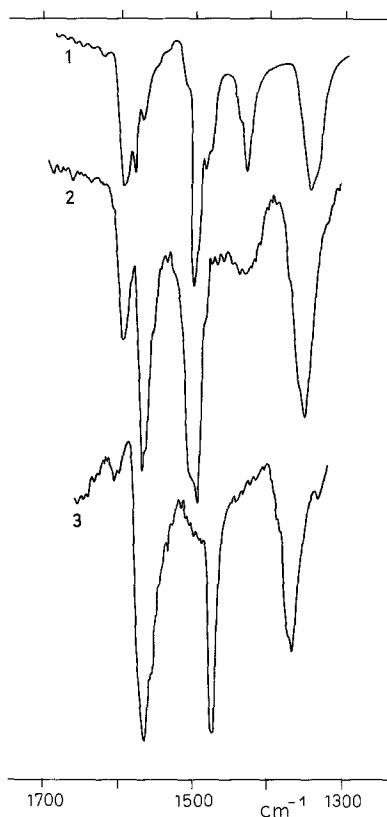

Fig. 3. IR spectra in the 1300–1700 cm^{-1} region: *1*,3-hydroxy-pyridine in D$_2$O solution; *2*,N-methyl-3-pyridone in D$_2$O solution; *3*,3-hydroxy-pyridine mull of crystals in perchloro-fluoro-ethylene

of 3-hydroxy-pyridine Fig. 3. The similarity of the absorption pattern of its D$_2$O solution with that of the N-methyl-derivative in the same solvent is striking, and this we believe suggests the presence of a tautomeric equilibrium with the free basis in its oxo-form. Viceversa the enol structure seems to prevail in the crystal spectra.

The results which we have discussed so far could have been obtained much earlier had it not been for wrong interpretation of the classical formulae which led to a denial of the existence of β-pyridones. This circumstance has even pre-

vented a full appreciation of results which were published long ago. This is the case of 8-hydroxy-quinoline. Its N-methyl-derivative X was obtained in 1939 [22]
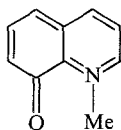
X

by reaction with diazomethane: it was shown to be different from the O-methyl ester, but the possibility of it being the N-methyl ester was not even mentioned by the authors. This, however, was recognized in 1944 [23] and the compound formulated as a zwitter-ion. The work was repeated and the structure confirmed in 1951 [24], and the case was fully discussed in 1959 by Saxena, Stafford and Stafford [25]. They classified the compound as the anhydrosalt of a betaine and stressed its relationship to β-pyridone but failed to recognize that their result was a good point against the doubts spread in the literature about the possibilty of its existence [1–4].

The same misunderstanding, in our view, led to the establishment of the class of the so-called "mesoionics", regarded as peculiar because of their lacking a covalent bond representation in terms of the electron pairing scheme where one such "bond" corresponds to each "line" between two atoms. This well defined scheme of electron pairing is characteristic of a certain approach used in the valence bond (VB) method for building molecular wave-functions, but it is not strictly necessary, and in fact not generally required, as it happens, e.g., in any version of the molecular orbital (MO) method.

The peculiarity of "mesoionics" derives from an *assumed* relationship between the structural formula representing the molecule and the VB method adopted for the construction of its wave-function. This assumption and the revision of the chemical symbolism which followed [26] were not without difficulties [27], but remained embodied in the theory of chemistry because of the historical privilege of VB "structures" of being used very early to calculate the hamiltonian "... matrix elements for the Lewis electronic structure of molecules" [28]. When it is recognized that the association of a VB determinant with *one* given classical formula is not necessary [1], the classical formulae can be left unaltered, and taken for what they were meant to be in the past.

We have proposed previously [9], as an addition to their meaning, the correlation of the symbolic notation of atoms in molecules, e.g. $=C\diagdown$, $-C\equiv$, $-N=$, $=O$, etc., with the respective valence states $C(tr\,tr\,tr\,\pi,\ V_3)$, $C(di\,di\,\pi\,\bar{\pi},\ V_2)$, $N(tr^2\,tr\,tr\,\pi,\ V_2)$, $O(tr^2\,tr^2\,tr\,\pi,\ V_1)$ etc. This correlation adequatly reflects the electronic structure of the molecules, is independent of the method chosen for constructing the molecular-wave-function, and offers a coherent systematization of the symbolism which we have used to discuss the case of β-pyridone. Whichever

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[1] Alternative procedures are available which do not need the "structure" representation of the VB basis set [29]. The circumstance that the VB determinant corresponding to "structures" like II, III, X is zero does not imply that the corresponding formulae are wrong, but only requires the introduction in the basis set of determinants associated with charge separation or "ionic structures".

name and formulation will be addopted, VII or VIII, all that needs to be shown in the formula is the n-coordination index of the valence state, V_n, which is sufficient to represent the space arrangement of the atoms. To add the classical symbols has the advantage, as exemplified before [30], of qualitatively indicating a certain degree of electron delocalization, or of charge polarization, whichever the case. The remaining quantitative aspects of electron distribution have to be obtained from the molecular wave-function.

Appendix

Theoretical

The geometry adopted for the molecules is shown in Fig. 4. The hydroxy-pyridines were all given the same ring bond lenghts and angles as pyridine itself [31, a], with an average C–OH distance 1.35 Å. The pyridones were given dimensions derived from those of the N-methyl-2-pyridone [31, b]. The bond of the substituent group was assumed to bisect the external angle of the ring.
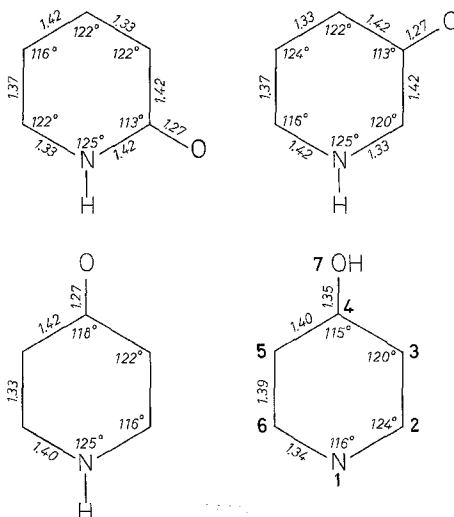

Fig. 4. Molecular geometry adopted for pyridones and hydroxy-pyridines

The α_p^{core} integrals were calculated without introducing the penetration integrals because these have been shown in Part I [17] to have no influence on the ΔE_π energies defined by Eq. (1).

The coulomb repulsion integrals γ_{pp} and γ_{pq} for $R < 2.8$ Å were obtained according to the Pariser and Parr procedure as previously described [17]. The W_p and A_p values and the formulae have been reported by Paoloni and Ciampi [30]. The γ_{pq} for $R > 2.8$ Å were calculated from the Roothaan integral expansion.

The overlap integrals used for evaluating the β_{pq}^{core} integrals were calculated from the usual Slater nodeless $2p\pi$ functions, with the atomic effective charge appropriate to the molecular core.

Numerical values for the integrals S_{pq}, γ_{pq}, the eigenvalues and the eigenvectors need not be listed since they can be obtained from the information given through any computer and the programs made available by the Quantum Chemistry Program Exchange.

Experimental

Preparation of N-methyl-3-pyridone. The dimer of N-methyl-3-hydroxy-pyridinium iodide, obtained as described by Mecklenborg and Orchin [19] is treated with an aqueous suspension of freshly precipitated silver oxide. The precipitate is filtered off, the clear solution is saturated with potassium carbonate, and the liquid which separates is dried at 100° C under reduced pressure.

The product is a yellow oil which solidifies in time and melts between 60 and 65° C. It gives a correct analysis for C_6H_7ON: calculated % C, 66.03; H, 6.47; N, 12.84; found % C, 66.0; H, 6.31; N, 12.7. It must be kept in a sealed tube to avoid darkening in the air.

Spectroscopic measurements. The IR spectra have been recorded with a Perkin-Elmer spectrophotometer Mod. 125, using sodium chloride or Irtran window cells. The D_2O solution spectra were corrected for the absorption of the solvent when this was required.

The p.m.r. spectra were recorded with a Varian A-60 instrument at room temperature, with tetramethylsilane as the external reference.

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