The Electronic Structure of Groups of Isomeric Heteroaromatic Systems

IV. Structure and Spectra of Pyridones and Their N-Methyl Derivatives

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Using the CNDO procedure, an all-valence electron study, including configuration interaction, was made of the three pyridone isomers and their N-methyl derivatives. The calculated dipole moments were found to be in reasonable agreement with the available experimental data, and the value predicted for N-methyl-3-pyridone was 7.2 D.

Transition energy, intensity and assignment were compared with ultraviolet spectra, recorded for the first time on all the N-methyl substituted isomers under similar conditions in non-aqueous solvents. The agreement is satisfactory for the 2- and 4-pyridone isomers, less so for N-methyl-3-pyridone.

Mit Hilfe der CNDO-Methode wurden die drei Pyridonisomeren und ihre N-methyl-Derivate untersucht. Die berechneten Dipolmomente sind in befriedigender Übereinstimmung mit den experimentellen Daten; der berechnete Wert für N-methyl-3-Pyridon war 7,2 D. Die berechneten Übergangsenergien, Intensitäten und Zuordnungen wurden mit dem experimentellen UV-Spektrum verglichen, das zum ersten Mal für alle N-methyl-substituierten Isomeren unter ähnlichen Bedingungen in nichtwäßrigen Lösungsmitteln aufgenommen wurde. Die Übereinstimmung ist zufriedenstellend für die 2- und 4-Pyridon-Isomeren, jedoch weniger gut für N-methyl-3-Pyridone.

On donne les résultats d'un calcul CNDO avec interaction des configurations, sur tous les électrons des pyridones isomères et leurs derivés N-méthylés. Les moments dipolaires calculés sont en bon accord avec les données expérimentales. La valeur 7.2 D est prévue pour le moment du N-méthyl-3-pyridone.

L'energie, l'intensité et les attributions des transitions calculées sont comparées avec les spectres d'absorption dans l'ultraviolet des N-méthyl-pyridones isomères. Ces spectres ont été mésurés sous des conditions rigueurésement comparables en solution non-aqueuse pour la prémière fois. L'accord est satisfaisant pour les derivés du 2- et du 4-pyridone, moins pour le derivé du 3-pyridone.

A previous comparative study of the π-electron structure of the three pyridone isomers [1] has shown that a substantial similarity was to be expected in their ground-state properties and, in particular, that there was no reason to doubt the existence of the isomer 3-pyridone and its derivatives. These conclusions were the starting-point for the work which led to the synthesis of N-methyl-3-pyridone, reported in the same paper [1].

A localization transformation of the π-electron MO's was described in a subsequent paper [2], and their analysis showed that the classic formulae are a realistic representation of the π-electronic structure of pyridones since the double-bond localization in I, II, and III agrees with the maximum π-electron localization of their MO's.
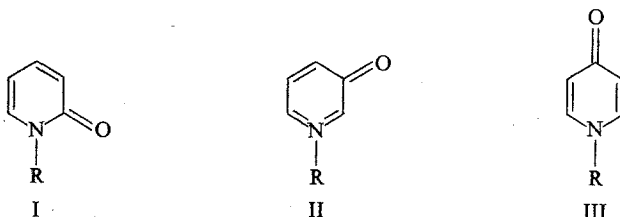
The present paper describes an all-valence electron study of the same compounds (R=H, CH$_3$), carried out for testing our previous conclusions [1] — based only on the π-electrons — and also for obtaining reliable predictions of their dipole moments and electronic transitions.

Within this scope we found it necessary to record the UV spectra of I, II, and III (R=CH$_3$) in non-aqueous solvents under comparable conditions. The spectra of the O- and N-methyl derivatives of the hydroxy-pyridine isomers seem in fact to have been studied mainly for identifying the tautomeric forms present in their aqueous solutions [3–8]. Thus, e.g., the spectrum of 3-hydroxy-pyridine methoiodide has been reported in aqueous solution at various pH's [6] and in neutral, acidic, and alkaline ethanol [5], and the spectrum of its methochloride has been studied in water, in dioxane[1], and in water-dioxane mixtures [4c].

These spectral data have been regarded by a number of authors as supporting the existence of a species of "salt-like character", the zwitter-ion [4] or phenol-betain [5] structure IV, with the stated [7] or implied presumption that the structure II could not exist, and with the extensive conclusion that the zwitter ion formulae represented the normal amido tautomers of this group of compounds [4, 8].

This interpretation of the spectral data is still widely accepted in the literature [9], and the writing of structure II is considered impossible as a matter of course [10].

Another object of the work here reported was, therefore, to see to what extent a formulation like IV can be based on a realistic evaluation of the molecular electron density distribution.
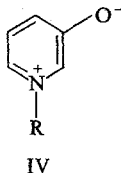
Method of Calculation

The MO's of the isomers I, II, and III (R = H, CH$_3$), were obtained by the CNDO procedure [11] extended by configuration interaction as proposed by Del Bene and Jaffé [12]. The program, based on their parameters and including the lowest 40 mono-excited configurations, was made available to us by Professor Leibovici, to whom we express our thanks. The computation of the ground-state properties, also carried out with the CNDO/2 program – written by Segal (QCPE n. 91) – gave equivalent results.

Three different rotational positions of the methyl group were considered for each isomer in order to examine the influence of N-methyl substitution and to determine the configuration of lowest energy. The ring bond lengths and angles were the same as in Ref. [1]. For other details see the Appendix.

Results

A. Ground State

The molecular charge diagrams of pyridones and their N-methyl derivatives, given in Fig. 1, show that the nitrogen atom bears a small negative charge in all compounds except the 3-pyridones, whose nitrogen is positively charged. However, this electron deficiency, about $+0.1$, is 2.5–4 times smaller than that of the carbon atom bound to the substituent oxygen. This latter possesses in all cases a negative charge of about 0.5 e.
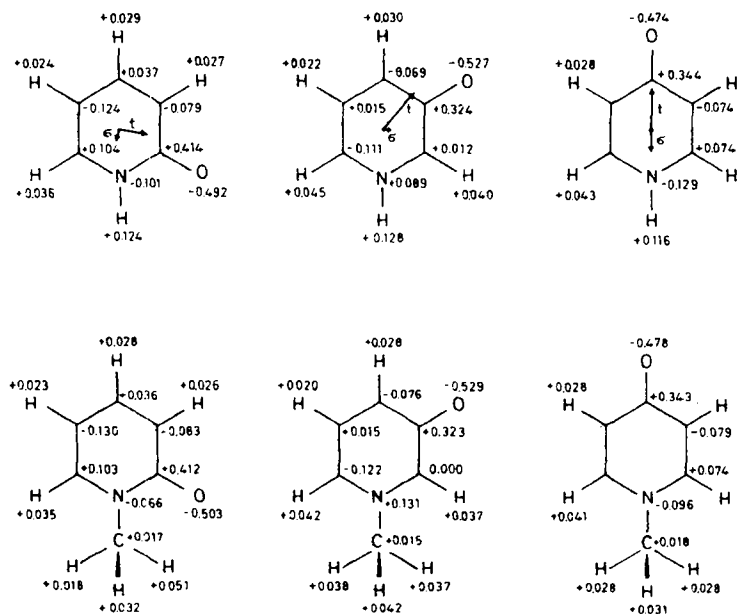

Fig. 1. Net total charges, total dipole moment and its μ_a component of pyridones and their N-methyl-derivatives
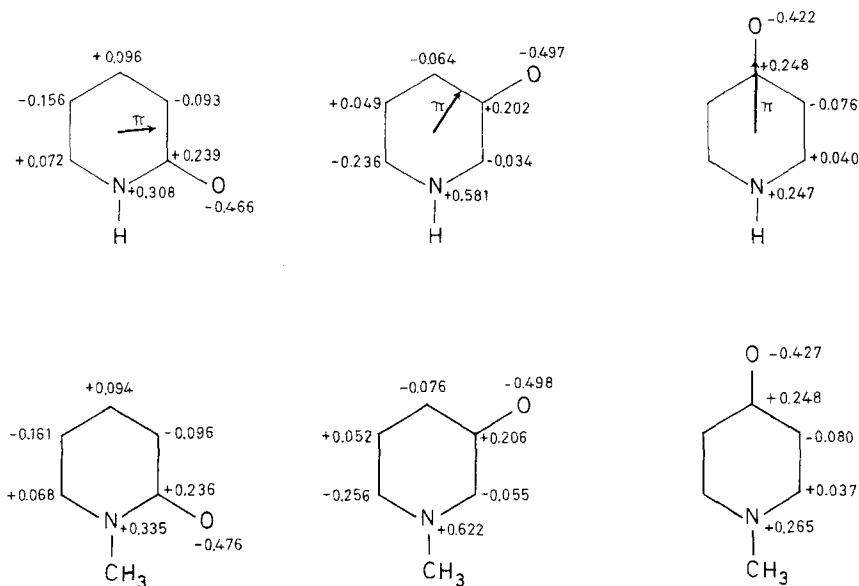
Fig. 2. Net π-charges and μ_π component of dipole moment of pyridones and their N-methyl derivatives

The total net charges are the result of a complex balance that can be seen by examining separately the contribution of the π-electrons, shown in Fig. 2. The negative charge of the extracyclic oxygen derives almost entirely from the π-electron migration. The small contribution, 5–10%, from the σ-electrons increases in the order 2- < 3- < 4-pyridone, and seems not affected by the N-methyl substitution. The π-electron loss of the nitrogen atom in the 2- and 4-pyridone isomers is smaller than the negative charge due to the σ-electron migration. This migration is the largest with 3-pyridone, about 20% greater, but it is not sufficient to compensate for a π-electron loss nearly double of that occurring in the other isomers.

An interesting point is that the largest negative charge in the pyridine ring is located on the carbon atom *para* to the substituent oxygen. This negative charge results from the accumulation of π-electrons which is neutralized only in part (20% for C (5) in 2-pyridone and 50% for C (6) in 3-pyridone) by the loss of σ-electrons. This net π-migration on the ring position *para* to the oxygen atom might explain why the 4-pyridone nitrogen shows the lowest π-electron vacancy and the 3-pyridone nitrogen the highest π-electron vacancy: the π-migration brings in a compensation in the first molecule and an accumulation of the π-electron losses in the second.

This analysis of the molecular electron distribution shows that the zwitter-ion formulae, like IV, approximately represent the polarization of the π-electrons in the oxygen and nitrogen $p\pi$ atomic orbitals. However, a more realistic image of the molecular polarities, based on the total charges, should localize the positive charge on the carbon atom bound to the substituent oxygen, because it is the carbon end of the C=O group which loses both σ- and π-electrons and has therefore the largest electron vacancy in the molecule.

The molecular polarity is largely determined by the π-electron distribution. This follows from the comparison of the total dipole moments, reported in Table 1, and their σ- and π-components, shown in Figs. 1 and 2. The centroid of the positive charge is progressively displaced away from the nitrogen atom when the substituent oxygen moves to the positions 2, 3 and 4.

Table 1. Calculated and experimental[a] dipole moments, D

R		2-oxo	3-oxo	4-oxo
H	μ_x	-4.78	-4.78	0
	μ_y	0.68	-5.78	-7.26
	$\mu_{tot.}$	4.83	7.49	7.26
	$\mu_{exper.}$	1.95	—	5.3
CH_3	μ_x	-4.76	-4.75	0
	μ_y	0.36	-6.28	-7.55
	$\mu_{tot.}$	4.78	7.88	7.55
	$\mu_{exper.}$	4.04	—	6.9

[a] See Ref. [13]. The experimental values of the R=H compounds do not represent the value of the isolated molecule because of strong hydrogen bonded association [17] and solvent-solute interactions [18].

Table 2. Energy levels of pyridone isomers and their N-methyl derivatives, eV

	2-oxo		3-oxo		4-oxo	
	NH	NMe	NH	NMe	NH	NMe
π	2.714	2.812	3.110	3.242	3.124	3.208
π	0.804	0.884	0.782	0.909	0.411	0.481
π	-0.300	-0.186	-1.211	-0.936	-0.159	-0.013
π	-9.769	-9.608	-8.825	-8.715	-9.870	-9.657
n	-11.206	-11.043	-10.165	-10.030	-10.445	-10.343
π	-12.880	-12.429	-12.610	-12.370	-11.944	-11.862
π	-13.781	-13.636	-14.199	-13.745	-14.329^{a}	-13.779
σ	-14.221	-14.079	-14.209	-13.990	-14.184^{a}	-13.995
σ	-14.663	-14.433	-14.621	-14.463	-14.908	-14.702
σ	-16.590	-16.106	-16.772	-16.397	-16.768	-16.338^{a}
π	-17.523	-16.215	-17.576	-16.468	-17.171	-16.268^{a}
σ	-18.142	-16.688	-17.720	-16.889	-17.564	-16.488
σ	-18.686	-17.559	-19.042	-18.145	-18.864	-18.195
σ	-19.886	-18.727	-20.270	-18.479	-20.130	-18.778
π (Me)	—	-19.911	—	-20.426	—	-19.967
σ	-22.861	-20.475	-22.783	-20.744	-22.795	-20.787
σ	-26.888	-22.237	-26.864	-22.285	-26.584	-21.165
σ	-27.684	-25.189	-28.162	-25.527	-27.174	-26.255
σ	-32.310	-27.871	-31.826	-27.598	-33.746	-27.768
σ	-37.202	-30.920	-36.877	-30.895	-34.864	-28.919
σ	-42.000	-32.425	-43.038	-32.922	-42.945	-34.983
σ	-47.485	-39.039	-47.434	-38.347	-46.754	-36.561
σ		-42.068		-43.359		-43.408
σ		-48.304		-48.068		-47.298

[a] σ and π assignment reversed with respect to the other isomers.

Table 3. Singlet-singlet electronic transitions of pyridone isomers and their N-methyl derivatives

R	ΔE, eV	f	Polarization		Assignment[a]	
			x	y		
2-oxo						
H	3.78	0	—	—	$n \rightarrow \pi^*$	
	4.19	0.11	−0.83	−0.56	$\pi \rightarrow \pi^*$	
	5.37	0.18	−0.73	0.68	$\pi \rightarrow \pi^*$	
	5.88	0	—	—	$n \rightarrow \pi^*$	
CH$_3$	3.78	0	—	—	$n \rightarrow \pi^*$	
	4.15	0.10	0.79	0.61	$\pi \rightarrow \pi^*$	
	5.28	0.16	0.76	−0.65	$\pi \rightarrow \pi^*$	
	5.82	0	—	—	$n \rightarrow \pi^*$	
3-oxo						
H	3.00	0.11	−0.90	0.44	$\pi \rightarrow \pi^*$	
	3.17	0	—	—	$n \rightarrow \pi^*$	
	3.91	0	—	—	$n \rightarrow \pi^*$	
	4.45	0.14	−0.84	−0.54	$\pi \rightarrow \pi^*$	
CH$_3$	3.06	0.11	−0.89	0.45	$\pi \rightarrow \pi^*$	
	3.22	0	—	—	$n \rightarrow \pi^*$	
	3.95	0	—	—	$n \rightarrow \pi^*$	
	4.45	0.13	−0.85	−0.52	$\pi \rightarrow \pi^*$	
4-oxo						
H	3.01	0	—	—	$n \rightarrow \pi^*$	A_2
	4.51	0.011	1	0	$\pi \rightarrow \pi^*$	B_2
	5.09	0.26	0	1	$\pi \rightarrow \pi^*$	A_1
	5.30	0	—	—	$n \rightarrow \pi^*$	B_1
CH$_3$	3.04	0	—	—	$n \rightarrow \pi^*$	A_2
	4.41	0.016	1	0	$\pi \rightarrow \pi^*$	B_2
	4.96	0.26	0	1	$\pi \rightarrow \pi^*$	A_1
	5.27	0	—	—	$n \rightarrow \pi^*$	B_1

[a] The transitions of the 4-pyridone isomers are labelled also with the C_{2v} irreducible representations of the excited state.

The experimental dipole moments of N-methyl-2-pyridone and N-methyl-4-pyridone, measured in benzene solution, are [13] 4.04 and 6.9 D respectively, about 0.7 D smaller than the calculated values. If this difference is regarded as due to the approximations of the method, then the best prediction for the N-methyl-3-pyridone dipole moment is 7.2 D.

The sequence of the energy levels, shown in Table 2, is the same for all the isomers, with minor differences for the 4-pyridone compounds. The highest occupied MO is of π-character, but the next below is largely localized on the non-bonding AO of oxygen. The lowest occupied π MO of the N-methyl derivatives has its population mainly distributed on the methyl group. The so-called hyperconjugation is therefore embodied in the procedure, and the non-symmetric orientation of the methyl group is favoured with respect to those orientations which have one hydrogen atom lying in the plane of the ring. The energy gain due to methyl rotation (see Table 4) is 0.19, 0.13, and 0.32 (or 0.54, 0.20, and 0.32) eV

Table 4. Total energies of pyridones and their N-methyl derivatives, eV

N-substituent[a]	2-oxo	3-oxo	4-oxo
H	− 858.92	− 855.57	− 863.41
CH$_3$, 0°	− 933.98	− 936.56	− 944.76
+ 90°	− 933.79	− 936.43	− 944.44
− 90°	− 933.44	− 936.36	− 944.44

[a] The 0° angle of methyl group corresponds to a C−H bond in the plane perpendicular to the ring plane. Rotation is negative towards the side of the oxygen atom.

respectively, for each conformation of the 2-, 3-, and 4-pyridone isomers. The charge distribution is only slightly affected by the rotation of the methyl group, and the alteration of the dipole moment is negligible ($\simeq 0.02$ D).

B. Excited States

The four lowest calculated singlet-singlet transitions and their assignment is shown in Table 3. The 2-oxo and the 4-oxo isomers show the same pattern: a lowest $n \rightarrow \pi^*$ followed by two $\pi \rightarrow \pi^*$ transitions. This sequence changes in the 3-oxo isomer, where the lowest $\pi \rightarrow \pi^*$ is followed by two $n \rightarrow \pi^*$ transitions.

The N-methyl substitution has a small effect, bathochromic on the $\pi \rightarrow \pi^*$ and negligible or hypsochromic on the $n \rightarrow \pi^*$ transitions of the 2-oxo and 4-oxo isomers. The same substitution appears to have an hypsochromic effect on all the transitions of the 3-oxo isomer.

The comparison of the calculated transitions with the recorded spectra is shown in Fig. 3. The agreement is very satisfactory for the position and relative intensity of the N-methyl-2-pyridone spectrum. The experimental assignment based on the band shift in aqueous solutions, seems to correspond with that deduced from the transition moment and the electron population analysis.

The calculated $\pi \rightarrow \pi^*$ transitions of the N-methyl-4-pyridone compare very well with the observed bands. Reasonable evidence for the $n \rightarrow \pi^*$ transitions predicted at 5.30 eV is the remarkable difference between the absorption intensity of the H$_2$O and that of the NaOH solutions in the 45000 cm^{-1} region. The lowest $n \rightarrow \pi^*$ is however predicted at about 24000 cm^{-1} (400 nm), a region where we have not found any appreciable absorption down to $\varepsilon \simeq 10$.

The agreement is relatively poor with the spectrum of the N-methyl-3-pyridone, whose lowest calculated transition, predicted $\pi \rightarrow \pi^*$, falls just outside the first absorption band, whose prevailing character is $n \rightarrow \pi^*$. It is possible that a marked hypsochromic shift of this band may be due to a strong dipole-dipole interaction with acetonitrile. The spectra of the liquid film and of the saturated solution in cyclohexane (5 cm, unknown concentration) show a pronounced shoulder at 390 nm and the maximum is displaced to 365 nm.

There are no spectral data to be compared with the singlet-triplet transitions listed in Table 5. Although these predictions are in general less reliable than those for the singlet-singlet, it is remarkable and, we believe, significant that 3-pyridone
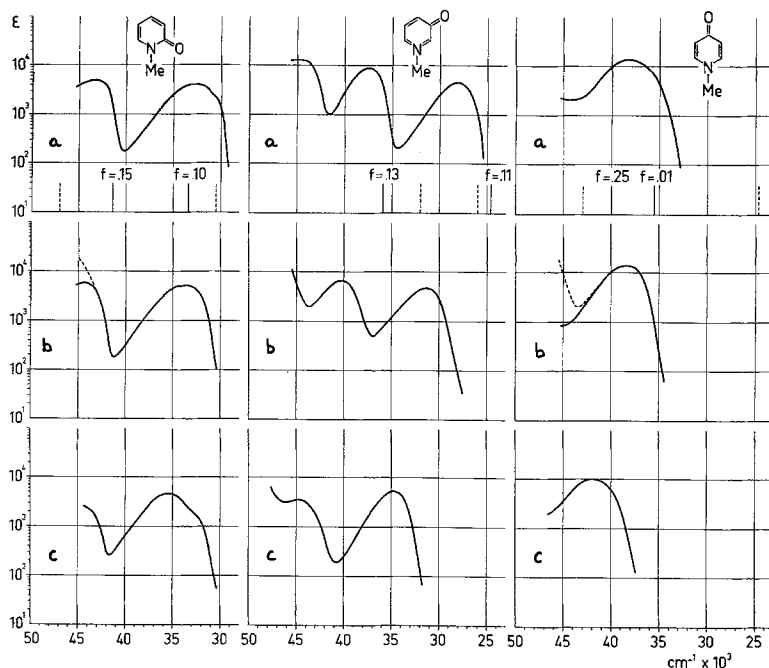
Fig. 3 a—c. Absorption spectra of N-methyl pyridones. Solvents: a Acetonitrile; b —— water; - - - - 0.1 N NaOH; c 0.1 N HCl. The calculated transitions and their oscillator strengths f are shown on the base-line of a. The broken lines mark here the forbidden transitions

Table 5. Singlet-triplet electronic transitions of pyridone isomers and their N-methyl derivatives, eV

N-substituent	2-oxo		3-oxo		4-oxo	
H	2.47	$\pi \to \pi^*$	0.89	$\pi \to \pi^*$	2.76	$\pi \to \pi^*$
	3.48	$\pi \to \pi^*$	2.96	$n \to \pi^*$	3.02	$\pi \to \pi^*$
	3.78	$n \to \pi^*$	3.17	$n \to \pi^*$	3.02	$n \to \pi^*$
CH_3	2.49	$\pi \to \pi^*$	1.00	$\pi \to \pi^*$	2.74	$\pi \to \pi^*$
	3.46	$\pi \to \pi^*$	2.98	$n \to \pi^*$	2.99	$\pi \to \pi^*$
	3.80	$n \to \pi^*$	3.22	$n \to \pi^*$	3.05	$n \to \pi^*$

and its N-methyl derivative should absorb in the near infrared, having their lowest triplet level lowered towards the ground-state by a factor of 2.5 or 3 compared with the other isomers. This circumstance could be related to the rapid alteration of the compound when, even for a short time, it is heated above 100° C.

    The analysis of the electron distribution of the singlet excited states reveals several interesting features mainly concerning the C=O group and the nitrogen atom. The polarization induced by the $\pi \to \pi^*$ transitions causes a shift of 0.3—0.5 e within the π-orbitals but leaves unchanged the ground state σ-electron distribution. In all compounds the $\pi \to \pi^*$ transitions occur with a net transfer of π-electrons from the extra-cyclic oxygen to the ring atoms, and the corresponding reduction

of the negative charge on oxygen varies from 0.1–0.25 e. The nitrogen $2p\pi$-orbital population of the 2-oxo and 4-oxo compounds is also reduced by the $\pi \to \pi^*$ transitions and the net negative total charge of the ground state is reversed in some cases. The opposite occurs in the 3-oxo compound, where the $2p\pi$ nitrogen population is increased and the net positive charge of the ground state reversed because the balance now gives about -0.15. Therefore as a consequence of the $\pi \to \pi^*$ transitions the electron vacancy of the nitrogen $2p\pi$-orbital is increased in the 2-oxo and 4-oxo, and decreased in the 3-oxo compounds.

About 75 % of the $n \to \pi^*$ transition electron transfer comes from the in-plane $2p$ orbitals of oxygen, whereas its $2s$ population remains nearly constant at about 1.72 e, for all the isomers. As a consequence, the oxygen atom acquires a net positive charge of about 0.15. The simultaneous change of the ring core polarization is rather small, with shifts never larger than 0.08 e on a single orbital. The n-electron migration from oxygen is partly balanced by a donation to its $2p\pi$-orbitals, whose negative charge increases by about 0.05 in the 3-oxo to a maximum of 0.15 in the 4-oxo compound. The nitrogen $2p\pi$-orbitals receive the largest share of n-electrons in the 3-oxo compound, which in the $n \to \pi^*$ excited states acquires on nitrogen a negative net charge comparable to that of the other isomers. More uniformly, the strong positive charge of the C=O-group carbon atom in all isomers is reduced to about half of its ground state value.

Discussion and Conclusions

Our previous calculations [1], based on the π-electrons only, suggested that 2-pyridone was the most stable among the three isomers. The total energies of our present calculations, including all the valence electrons (Table 4), indicate 4-pyridone as the lowest-energy isomer. In both cases 3-pyridone is the intermediate term in the series.

It should be stressed, however, that the comparison cannot be decisive because of the uncertainties in the bond angles and distances, which were assigned average values, based on the data available for N-methyl-2-pyridone and similar molecules[2].

Concerning more specifically the case of 3-pyridones and the structural peculiarities that the experimental chemists have assigned to it [7, 8], we think it convenient to collect here several theoretical peculiarities, which might be typical of these compounds:

i) the total π-orbital of the ring nitrogen shows the largest π-vacancy (about 0.6); the migration of σ-electrons, which is sufficient to make the nitrogen of the other isomers negative, leaves the atom slightly positive;

ii) the compound has the largest dipole moment, where the σ-component adds to the π-component with an increasing instead of a decreasing effect;

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[2] For this same reason we have not made a comparison between the total energies of the oxo- and hydroxy-tautomers. Establishing a stability sequence for isomeric molecules with atoms of different valence state is likely beyond the limit of reliability of the CNDO procedure, unless the dimensional parameters of the molecules are known.

iii) its lowest singlet-singlet transition is predicted $\pi \to \pi^*$, and not $n \to \pi^*$ as in the other pyridones;

iv) its lowest singlet-triplet transition is in the near infrared;

v) its ionization potential, as measured by the energy of the highest occupied MO is nearly 1.0 eV lower than that of the other terms.

Although the spectral predictions regarding 3-pyridone and its N-methyl-derivative are apparently less reliable than the others here made[3], we believe that the whole results show that 3-pyridone should be affected by radiation, heat or reagents much more easily than its isomers.

The method of calculation is another aspect of our results which requires a few comments. The data we have discussed so far have been obtained by using the Pariser-Parr formulae for the γ_{pq} integrals. The alternative use of the Nishimoto-Mataga procedure leads to minor differences in the charge distribution of the ground state. Marked differences are found instead for the excited state. The lowest transition is always red-shifted by 0.2—0.4 eV; the others are less affected. For comparison we report here the transitions calculated for N-methyl-3-pyridone: 2.84 eV $(f = 0.0\ n \to \pi^*)$; 3.10 $(f = 0.11, \pi \to \pi^*)$; 3.71 $(f = 0; n \to \pi^*)$; 4.47 $(f = 0.16, \pi \to \pi^*)$.

The $n \to \pi^*$ transitions are the most affected by the Nishimoto-Mataga γ_{pq} integrals, and the result seems worst with respect to the spectral data: e.g., for N-methyl-2-pyridone 3.41 eV $(f = 0, n \to \pi^*)$, to be compared with 3.78 eV in Table 3. Moreover, the Nishimoto-Mataga integrals slow down the convergence, increasing the computing time by a factor of about 10.

A final comparison can be made with the Pariser-Parr-Pople, π-electron method. The molecular diagrams (Fig. 2) are similar to those of our previous work [1][4]. The spectral predictions, based on 12 monoexcited configurations, which were not published at that time, gave the lowest $\pi \to \pi^*$ at 4.92, 3.77, and 4.88 eV, respectively, for 2-, 3-, and 4-pyridone. The corresponding transitions in Table 3 are 5.35, 3.02, and 4.51 eV, within accepted limits of approximation for the 2-oxo and the 4-oxo-compounds.

Appendix

Theoretical

The following additions have to be made to the geometry adopted in Ref. [1]: ring C—H: 1.075 Å; methyl C—H: 1.09 Å; N—H: 1.02 Å; and N—CH$_3$: 1.48 Å.

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[3] An explanation of this apparent failure of the method may be found in the uncertainties of the dimensional parameters of the molecule, which might differ significantly from those we have assumed. Moreover, the CNDO approximation might fail with a high polar molecule because the core polarization accounted for in the procedure can be inadequate [14].

[4] In that paper we observed a quantitative relationship between the nitrogen net π-charge and the relative displacement of the methyl proton magnetic resonance absorption. We have now measured the PMR shift of N-methyl-4-pyridone: PPM 3.07 in $(CD_3)_2CO$; 3.64 in D_2O; 3.76 in $D_2O + NaOD$, and 4.13 in $D_2O + DCl$. Comparison of these with the previous data [1] shows that the qualitative trend with the net π-charges is maintained, although the relationship does not hold.

Experimental

Preparation of N-methyl-3-pyridone has been somewhat modified with respect to Ref. [1]. The liquid which separates after saturation with potassium carbonate was repeatedly extracted with acetone, which was then evaporated from the extract in the shortest possible time. The residue was maintained at 95–100° C at reduced pressure ($\simeq 10$ mm Hg) during 30 min. All these operations were performed away from light to avoid any photochemical alteration of the product [5]. N-methyl-3-pyridone thus obtained with better yield was identical in all respect to the material previously described and more suitable for recording UV spectra.

N-methyl-4-pyridone was obtained by methylation of the 4-pyridone according to the procedure of Ruzicka and Fornasir [16]. The free base was purified by repeated distillation of the product in a vacuum line and kept in a sealed tube.

The commercial N-methyl-2-pyridone (Schuchardt, München) was purified by distillation at reduced pressure and immediately used for recording the spectra.

The IR, the PMR spectra and the analysis of the products were consistent with their structure and in agreement with those reported in the literature.

Ultraviolet spectra were recorded using a Cary Md. 11 M.S. instrument, with spectrograde solvents checked before their use.

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[5] The acetone solution of the compound becomes blue when exposed to light, and the colour deepens to violet, and a brown oil separates, after prolonged exposure. The thin layer chromatography of this oil shows that it contains about 50% of the starting material and another component which has not yet been identified. Photochemical reactions have been reported also for the 2- and the 4-pyridone [15].

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