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PHOTOCHEMISTRY OF HETEROCYCLIC AROMATIC N-OXIDES VI (1)
A CNDO-CI ANALYSIS OF GROUND AND EXCITED STATE PROPERTIES OF PYRIDINE-N-OXIDE

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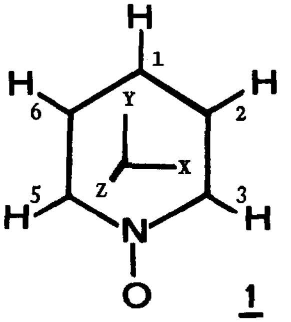
In connection with the photochemical behaviour of pyridine-N-oxide 1, and of its derivatives, which have been investigated by us and by others (1,2), we undertook a semi-empirical study of the ground state and excited state properties of pyridine-N-oxide itself. The quanto-chemical approach, which is being used throughout this preliminary work, is based upon the CNDO-CI method as modified by Del Bene and by Jaffe (3); this mathematical model permits an interpretation of the absorption spectrum of pyridine-N-oxide 1 . Having no experimental data of the geometry of 1 at hand, we postulate the following bond lengths and bond angles (Table 1)



1

d (C-N) = 1.40 Å
d (N-O) = 1.28 Å
d (C-C) = 1.40 Å
d (C-H) = 1.08 Å

All angles = 120°

TABLE 1 Assumed geometry of pyridine-N-oxide 1

MOLECULAR ORBITALS

Given the preceding geometry for pyridine-N-oxide 1, we obtain the following energy values for some characteristic molecular orbitals, the nature of the M.O.'s being indicated in brackets (Table 2).

Highest occupied M.O.'s			Lowest vacant M.O.'s		
Ψ_{14}	(σ)	-14.61 eV	Ψ_{19}	(π^*)	-0.64 eV
Ψ_{15}	(π)	-13.99	Ψ_{20}	(π^*)	-0.45
Ψ_{16}	(π)	-11.67	Ψ_{21}	(π^*)	+2.01
Ψ_{17}	(n)	-11.16	Ψ_{22}	(σ^*)	+3.78
Ψ_{18}	(π)	- 9.50	Ψ_{23}	(σ^*)	+4.56

TABLE 2 Energy levels of some characteristic M.O.'s of 1

The empirical relationship [1] between the first ionization potential and the energy values for the various M.O.'s has been proposed recently by one of us (4):

$$IP = -\epsilon_{N/2} + \Delta \qquad [\ 1\ ]$$

N being the total number of valence electrons and Δ a correction factor which is taken equal to -0.9 ± 0.2 eV. Making use of this equation, the first ionization potential for the promotion of a π electron of pyridine-N-oxide would be 8.6 ± 0.2 eV . We notice the pronounced lone pair character of M.O. Ψ_{17} at the oxygen atom as can be seen from the following relationship [2]:

$$\Psi_{17} = 0.93\ [\ 2p_x(O)\ ] - 0.22\ [\ 2p_x(N)\ ] \qquad [\ 2\ ]$$

As a consequence of the highly localized $2p_x$ A.O. at oxygen (86.5 %), the n-π^* transition should be strongly forbidden (5).

CHARGE DISTRIBUTIONS AND DIPOLE MOMENT OF PYRIDINE-N-OXIDE IN THE S_0 STATE

In order to check the validity of the postulated geometry of 1, we computed its total dipole moment μ. The dipole moment being the most sensitive property when changing some geometrical parameters, we shall see that our molecular model is correct; SCF-charges are reproduced in Table 3 . From these charge distributions one obtaines:

$$\begin{array}{lll} \mu_{at} = +\,4.02 \text{ Debyes} & (\text{ valence dipole distribution }) & \\ \mu_{sp} = +\,0.76 \text{ ''} & (\text{ atomic dipole distribution }) & \\ \hline \mu_{tot} = +\,4.78 \text{ ''} & & [\ 3\ ] \end{array}$$

Experimentally one finds:

$$\mu_{ex} = + 4.78 \text{ Debyes} \pm 0.07 \qquad (6)$$

Atom	A.O. Charges				Total Charge
	2s	$2p_x$	$2p_y$	$2p_z$	
C-1	1.028	0.988	0.988	1.054	4.058
C-2	1.039	1.005	1.003	0.957	4.004
C-3	1.031	0.908	0.963	1.124	4.026
N	1.170	1.133	1.084	1.140	4.526
O	1.770	1.993	1.160	1.644	6.566
	H-1 0.970		H-2 0.963		H-3 0.948

TABLE 3 Ground State charge distribution of pyridine-N-oxide

SINGLET EXCITED STATES

Taking in account the 30 lowest monoexcited singlet states, and starting with the SCF-MO's obtained previously, we have computed the electronic absorption spectrum of pyridine-N-oxide (Table 4). We notice good to excellent agreement between the calculated and the observed parameters for the four transition bands which are being observed. The first transition $\epsilon = 3.81$ eV is assigned to the lowest π-π^* excitation, a result which agrees well with some recent theoretical and experimental conclusions found for pyridine-N-oxides (7,8,9).

Theoretical Values				Experimental Values		
Δ E	f	nature	Pol.	Δ E	f	Pol. (8)
2.98 eV	0.00	n-π^*	Z			
3.76	0.03	π-π^*	X	3.81 eV	0.02	X
3.94	0.15	π-π^*	Y	4.40 eV	0.21	Y
5.62	0.00	n-π^*	Z			
5.92	0.25	π-π^*	X	5.72 eV	0.20	
6.05	0.14	π-π^*	Y			
6.56	0.40	π-π^*	Y	6.60 eV	0.25	

In agreement with Jaffe's results (10) an n-π* transion would be predicted to occur at about 3 eV , i.e. at a somewhat lower energy than the first π-π* transition; it should be forbidden as a consequence of the highly localized $2p_x$ A.O. at oxygen.

The overall dipole moments for the first excited singlet states have been computed in order to explain the observed solvent effects upon the absorption spectrum of pyridine-N-oxide (11). One of us has showed previously that a decrease of the total dipole moment of the excited states induces a blue shift (12); table 5 indicates the μ values obtained for some singlet states of compound 1. In the two π-π* states of lower energy (S_2^* and S_3^*) the dipole moment is strongly reduced,a prediction which agrees well with the blue shift which has been observed by Kosower (13) and by us (11). As a a matter of fact it seems that only the S_0-S_5 transition,which is observed at 217 nm (5.72 eV) is slightly red-shifted with an increase of the solvent polarity. Turning now our attention to n-π* transitions leading to singlet states (S_1 and S_4) we recognize a drastic reversal of the direction of μ (Δ μ = -8.5 for the S_0-S_1 transition) a prediction which may account for the fact that this transition does not show up in solution.

Electronic states	S_0	S_1^*	S_2^*	S_3^*	S_4^*	S_5^*	S_6^*	S_7^*
Total μ (Debyeds)	+4.78	-3.73	+0.41	+1.34	-6.96	+5.78	+0.72	+1.44

Table 5 : Dipole moments of some singlet states of pyridine-N-oxide

Next we examined the nature and the importance of the intramolecular charge transfers in ground and excited states (Table 6). It is interesting to notice that, among the π-π* singlet states, S_2 and S_5 states correspond to high transfer bands; this agrees with Kubota's experimental conclusions (14).

TRIPLET STATES.

In order to compute the energies and the properties of the excited triplet states, we took again into account, as above for the singlet states, the interaction of the thirty lowest monoexcited triplets. As can be seen from table 7 the first triplet state, which is found to be a π-π* transition, shows up at high wavelength (744 nm); according to our calculations it would exhibit a very small charge transfer character (-0.041). From the value of the corresponding dipole moment we predict a blue shift in solution or in a solid matrix for the S_0-T_1^* .

States	Transfer	Transfer	Total transfer
S_o	+0.216	−0.308	−0.092
S_1	−0.170	+0.504	+0.334
S_2	+0.528	−0.307	+0.220
S_3	+0.269	−0.303	−0.034
S_4	+0.216	+0.692	+0.808
S_5	−0.090	−0.304	−0.394
S_6	+0.366	−0.261	+0.105
S_7	+0.370	−0.294	+0.077

Table 6 Charge transfer in singlet states. Positive values refer to charge transfer from the N–O group to the remaining part of the molecule. S_1 and S_4 derive from n–π* transitions.

States	Δ E	Nature	Pol.	Dipole moment
T_1	1.67 eV	π–π*	Y	+1.51 D
T_2	2.97	π–π*	X	−0.75
T_3	2.98	n–π*	Z	−4.14
T_4	3.90	π–π*	Y	−1.70
T_5	4.59	π–π*	Y	+7.01

Table 7 Triplet state properties of pyridine-N-oxide.

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