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The Electronic Structure of N-Methyl-3Pyridone and its Representation

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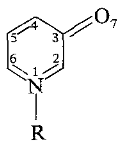
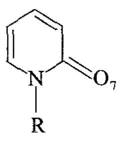
Quasi-localized MO's have been constructed for the π electron system of the three pyridone isomers.

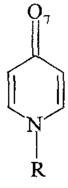
A recent PPP, ASMO, calculation has predicted that 3-pyridone should have properties similar to those of its 2- and 4-isomers, a result at variance with the belief that a structure corresponding to the classic formula I could not exist [1].



I



II



III

R = H, CH_3

As discussed before [1] this view derives from the circumstance that the Valence Bond (VB) determinant corresponding to I is zero. This however is the consequence of the particular electron coupling scheme adopted in the VB method and cannot be considered as the ground for such a conclusion since it is obvious that the "structures" associated with VB determinants do not have physical existence. It remained however to be established to what extent the formula I represented the actual electronic structure of the molecule. To clarify this point we have carried out a localization transformation of the Molecular Orbitals (MO) of the pyridone isomers used to derive our conclusion in Ref. [1]. The least-square procedure described by S. F. Boys [2] was used and the results are shown in the Table. Here the localized MO's are given, and the localization of each MO is measured by adding the square of its two largest AO coefficient (or by the square of the largest one, for localized pairs).

These results give evidence that the classic formulae of the pyridone isomers, I, II and III, represent a reasonable approximation to their actual electronic structure.

As a further comment to the data of the table it is interesting to remark that the electrons associated with the nitrogen doublet are localized in the lowest

Table. *Localized MO's and measure of bond localization*[a]

	2-Pyridone				3-Pyridone				4-Pyridone			
E_i in eV	−17.894	−13.824	−13.619	−13.284	−17.211	−15.076	−13.401	−12.551	−17.546	−13.636	−13.636	−12.866
AO 1	− **0.8828**	− 0.0282	0.0001	− 0.0601	**0.6679**	**0.4746**	0.1890	− 0.0351	**0.8988**	0.0328	0.0328	0.0556
2	− 0.2906	− 0.1623	− 0.2533	**0.4527**	**0.6816**	− 0.2031	− 0.1487	− 0.0174	0.2784	− **0.6406**	0.1280	−0.0685
3	− 0.0608	− 0.1100	− **0.7068**	− 0.0081	0.2167	− 0.1794	− 0.2998	**0.4620**	− 0.1058	− **0.7093**	− 0.0695	0.0065
4	0.0949	0.2518	− **0.6266**	− 0.0637	0.0647	− 0.0780	− **0.6982**	− 0.0286	− 0.1112	− 0.2353	− 0.2353	**0.4834**
5	0.1167	**0.7290**	− 0.0917	0.0528	− 0.1472	0.3354	− **0.5942**	− 0.0671	− 0.1058	− 0.0695	− **0.7093**	0.0065
6	− 0.3206	**0.6018**	0.1670	− 0.0098	− 0.1053	**0.7601**	− 0.0469	0.0714	0.2784	0.1280	− **0.6406**	0.0685
7	0.0844	0.0613	0.0853	**0.8857**	− 0.0741	0.0704	0.0978	**0.8801**	0.0499	0.0943	0.0943	**0.8682**
$\Sigma c^2_{\max}$	0.7793	0.8936	0.8922	0.9894	0.9107	0.8030	0.8405	0.9880	0.8078	0.9135	0.9135	0.9874
Bond	$\ddot{N}$	C=C	C=C	C=O	N=C	C=N	C=C	C=O	$\ddot{N}$	C=C	C=C	C=0

[a] Largest coefficients in each MO are in black type.

MO and those associated with the C=O group localized in the highest occupied MO. Moreover the main difference between 3-pyridone and its isomers seems to be the large "delocalization" of the nitrogen doublet towards the adjacent carbon atoms.

It is perhaps worth mentioning that this conclusion gives to the old controversy on pentavalent nitrogen [3] a historical perspective more fair to the supporters of classical formulae.

References

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