

Notes on the E.S.R. spectrum of hydrogenated pyridine

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(Received 25 September 1967)

The E.S.R. spectrum of irradiated pyridine has recently been reported by different authors [1, 2]. David *et al.* and Tsuji *et al.* obtained almost the same spectra for irradiated pyridine in solid state and confirmed that three kinds of radicals were produced. The triplet spectrum observed at 77°K was assigned by both authors to the pyridine cation radical produced by the removal of one electron from the nitrogen lone pair. The singlet spectrum observed at 221°K is identified by Tsuji *et al.* as the pyridyl radical. The spectrum observed at about 200°K, however, was assigned to different species of hydrogenated pyridine; namely, David *et al.* assigned to N-hydrogenated pyridine (N-Py), and on the other hand, Tsuji *et al.* to 3-hydrogenated pyridine (C-Py).

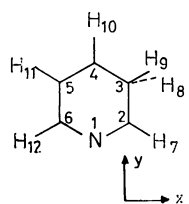
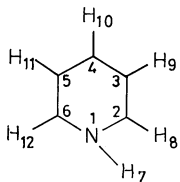
In order to settle this problem, we have calculated the electronic structures for both N-Py and C-Py radicals. The calculation was carried out by the semi-empirical unrestricted SCF-MO method, all the valence electrons being considered. The evaluation of matrix elements was made by the method developed by the present authors [3, 4], except for the off-diagonal core Hamiltonian matrix elements [5]. In actual calculation, we assumed that the hydrogen attaches to the 3-carbon atom or the nitrogen atom of pyridine with the tetrahedral angle and with the C-H bond distance of 1.09 Å and the N-H bond distance of 1.032 Å for C-Py and N-Py, respectively.

The total energy was calculated to be -932.25 and -935.66 eV for C-Py and N-Py, respectively†, and the calculated hyperfine coupling constants of both hydrogenated pyridines are summarized in the table. The observed coupling constant (24 G) was assigned by David *et al.* to 1-hydrogen of N-Py, and by Tsuji *et al.* to 8-hydrogen of C-Py. The present calculations seem to support the assignment by David *et al.* The coupling constants calculated for N-Py are in good agreement with the observed values. The hyperfine coupling constant, 54.6 G calculated for 8-hydrogen of C-Py is almost consistent with the observed [8] and calculated [9, 10] results for the cyclohexadienyl radical.

We may conclude from the above two reasons (total energy and calculated hyperfine coupling constants) that the E.S.R. spectrum of the irradiated pyridine observed at about 200°K may be due to the N-hydrogenated pyridine radical.

It may be interesting to discuss here the electronic structure of N-Py briefly. The highest occupied orbital (singly occupied orbital in the sense of restricted MO

† The single determinant used in unrestricted Hartree-Fock method is not generally the eigenfunction of the total spin angular momentum operator, S^2 , but it might not lead to serious error for the comparison of the total energy of two molecules composed of the same number of electrons [6].

Radical	Position	a , obsd. (G)	a , calcd. (G)
(1) C-Py 	N	—	2·13† —
	7	12	-11·2 (-10·0)‡
	8	24	56·4 —
	10	12	-15·2 (-11·7)
	11	—	8·13 (4·91)
	12	12	-15·2 (-11·9)
(2) N-Py 	N	12	9·37 —
	7	24	24·4 —
	8	12	-8·64 (-8·08)
	9	—	5·59 (3·45)
	10	12	-13·2 (-10·3)

† The proton hyperfine coupling constants are calculated by multiplying 508 G to the spin density on hydrogen atom, and the nitrogen hyperfine coupling constants are calculated by the empirical relation obtained by Ward [7].

‡ The values in parentheses are calculated from the spin densities on the carbon π -AO's using the McConnell relation ($a_{\text{H}} = -23\cdot04 \rho_{c_n}$).

Calculated hyperfine coupling constants (a 's) of
C-Py and N-Py radicals.

method) of N-Py is;

$$0\cdot11S_{\text{N}} - 0\cdot30P_{y\text{N}} - 0\cdot41P_{z\text{N}} + 0\cdot53(P_{z2\text{C}} + P_{z6\text{C}}) \\ + 0\cdot11(P_{z3\text{C}} + P_{z5\text{C}}) - 0\cdot58P_{z4\text{C}} - 0\cdot24h_7 + 0(0\cdot01),$$

where, 0(0·01) denotes the smaller term, the coefficients of which are in the range of 0·01 ~ 0·09.

The remarkable π -type conjugation is assured between the sp^3 -type AO's on the nitrogen atom and the π -type AO's of the carbon skeletons of N-Py. Further, the π -bond population of the C-N bonds in N-Py and pyridine are calculated to be 0·056 and 0·216, respectively. This shows that the double bond character of the C-N bonds in N-Py radical decreases remarkably. The C₂-C₃ bond in N-Py is, however, strengthened compared with that in pyridine; the π -bond population of C₂-C₃ bond in N-Py and pyridine are calculated to be 0·292 and 0·243, respectively.

The details of this study will be published in the near future.

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