

QUANTUM MECHANICAL CALCULATION ON THE REACTIVITY OF AZOLES AND AZINES

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INTRODUCTION

It has been shown by Wheland and Pauling (1935) that the calculated permanent charge distribution for a number of homocyclic and heterocyclic compounds, using molecular orbital method, can be satisfactorily correlated with the chemical reactivity of these compounds. Coulson and co-worker (1947, 1949) have extended this calculation to a large number of polynuclear hydrocarbons with hetero-atoms by essentially the same method (with modification in some cases), in correlating the reactivity with permanent charge distribution. In the present paper is reported the electron density calculations on azoles and azines and its correlation with chemical reactivity. These five and six membered hetero-rings bear to pyrrol and pyridine same relation as pyridine and pyrrol bears to benzene and corresponding hypothetical five membered homocyclic ring. These compounds are of interest to organic chemist because of their peculiar chemical reactivity and to bio-chemist for their interesting physiological properties.

METHOD OF CALCULATION

The method of calculation is too well known to reproduce here. The values of coulomb integral used in the present calculation are $E_0 + 2\beta$, $E_0 + 0.25\beta$ and E_0 for nitrogen, carbon bonded to nitrogen and carbon bonded to carbon respectively, β being the resonance integral which was taken to be equal for all bonds. The energy equations higher than second were solved by Pinch method correct up to

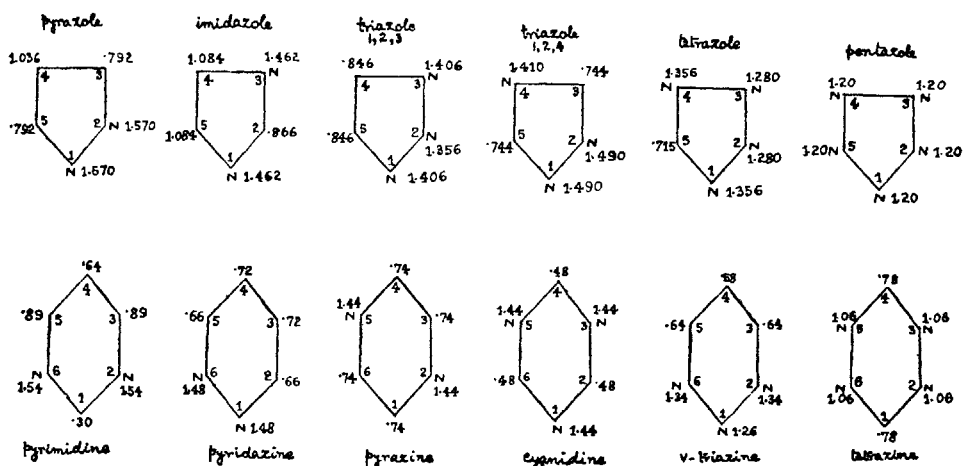


FIG. 1

first place. Π -electron densities for these compounds are shown in Fig. 1, against each atom. The numbering of the atoms is also given inside the ring.

DISCUSSION

It may be observed that the Π -electron density is rather high at 4 position in pyrazole so this position is highly reactive. Halogenation, nitration, and sulfonation take place at this position. Lesser electron density at the nitrogen atom makes this less basic than pyrrol. Imidazol, similarly, is less basic than pyrazole. Nitration and sulfonation proceed with equal ease at 4 and 5 positions of this compound. Bromination can cause substitution at all the carbon atoms. The substitution reaction at 2 position is most probably a secondary reaction, i.e. migration of the halogen atom from nitrogen to the carbon atom at 2 position (Morton, 1946). The reason for the assumption is two-fold. Firstly the hydrogen at 1 position can be replaced by bromine giving a tetrabromo compound. And secondly a methyl group from nitrogen does migrate to 2 position. 1, 2, 3-triazole is weakly basic. Rather low electron densities on carbon atoms in triazole makes this compound highly resistant to substitution reaction. Methyl groups at these positions are easily oxidized to give triazole carboxylic acid. Tetrazole is weakly acidic. Electron density at 5 position in tetrazole is extremely low, so the compound is easily attacked by alkali at this position. Pentazole, if it exists, will be extremely unreactive.

Compared to pyridine diazines are less basic, while triazines are less basic than diazines. Tetrazines are neutral or slightly acidic. Calculation agrees fairly well with this behaviour with the exception of pirimidine. High electron densities at the nitrogen atoms should make pirimidine basic. Actually the compound is a mono-basic acid. Extremely low electron density at 1 position may cause easy dissociation of the hydrogen atom at this position and this may account for its acidic character (Richter, 1923).

In pyrazine low electron densities at 2 and 5 positions make the compound susceptible to anionoid attack. Methyl substitution at these positions are easily oxidized to pyrazine carboxylic acid. In pirimidine, too, methyl substitution at 1 position is easily oxidized. Halogen atom at this position is replaced by NH_2 group by reaction with ammonia or sodamide. The mobility of halogen at 1 position in pirimidine is so great that it can be replaced by SCN by reaction with KSCN . Low electron densities at 2, 4 and 6 positions in cyanidine also makes the halogen atoms at these positions easily replaceable by NH_2 group. Methyl groups at these positions are easily oxidized to carboxylic acid. Low electron densities at the carbon atoms in azines make these compounds resistant to nucleophilic substitution, so these compounds do not undergo nitration, bromination or sulfonation.

SUMMARY

A quantum mechanical calculation of the electron densities at different positions of azole and azine molecules have been made and an effective correlation has been obtained with the chemical reactivity of the respective position.

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