On the First Ionization Energies of Heterocyclic Molecules

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(Received August 23, 1958)

In the present note the author wishes to show some results of semi-empirical estimation of the first ionization energies of π-electrons in heterocyclic molecules. The evaluation of these values was carried out according to Hush and Pople's method(1) in which electron interaction was taken into account explicitly.

The values of the integrals, resonance β_{pq}, one center electron repulsion $(pp|pp)$, and two center electron repulsion $(pp|qq)$, were taken from Pariser and Parr's paper(2), those of the first integrals for non-neighboring atoms p and q being neglected; it was assumed that Coulomb integral α_{cp} and resonance integral β_{pq} were identical for all carbon atoms and carbon-carbon bonds in the different molecules (see Table I) respectively. The interatomic distances in the molecules considered here were taken from electron diffraction data by Schomaker and Pauling(3).

With respect to the molecular orbitals, those obtained by the Hückel method were used as approximations, because in practice it is rather tedious to solve the self-consistent equation completely. The parameters of energy integrals in the Hückel method were chosen from Orgel et al.(4), except for all carbon atoms and the sulfur atom in thiophene. For the carbon the common value was taken (so-called α_c), and for the sulfur Longuet-Higgins' idea was employed. Furthermore electron densities of the carbon atoms were assumed to have equal values of those in alternant hydrocarbons, and the Coulomb integral was chosen to make the ionization energy computed for benzene equal to the experimental value.

In Table I are given the results, which are in good agreement with experiment, although many approximations were necessary through the calculation. It has been proposed that in pyridine and pyrazine the ionization energies of these compounds are largely determined by the non-bonding electrons on the nitrogen atom, from the studies of their methyl derivatives by electron impact method(6) and from the results of self-consistent calculation on these electrons(7). The energy interval of bombarding electrons, however, should be examined in the electron bombarding study, especially when the highest-occupied π-level may exist near nonbonding σ-levels. Details will be further discussed in subsequent publications.

TABLE I
RESULTS OBTAINED OF THE FIRST IONIZATION ENERGIES OF π-ELECTRONS, eV.

	calc.	obs.
benzene	9.24	9.24(8)
pyridine	9.45	9.76 ± 0.05(9), 9.23(10)
pyrazine	9.90	10.01 ± 0.02(6)
pyrrole	9.03	8.97 ± 0.05(9)
furan	8.94	9.00 ± 0.10(9), 8.89(10)
thiophene	9.34	9.1 ± 0.2(9)

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1) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

3) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).

4) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

5) H. C. Longuet-Higgins, ibid., **45**, 173 (1949).

6) I. Omura et al., This Bulletin, **30**, 633 (1957).

7) T. Nakajima and A. Pullman, *Compt. rend.*, **246**, 1047 (1958).

8) In the present report, this value was adopted as the most probable one; cf. J. D. Morrison, *J. Chem. Phys.*, **22**, 1219 (1954), K. Watanabe, ibid., **22**, 543 (1954).

9) H. Baba et al., This Bulletin, **29**, 521 (1956).

10) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).