Unstable Intermediates. The Electronic Structures of Benzynes and Hetarynes

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Benzynes are known to be typical unstable intermediates on the basis of many experimental results.1) Hetarynes, benzyne analogues derived from heteroaromatic compounds, such as 3,4-pyridyne,2),[*1] 4,5-pyrimidyne3) and 2,3-thiophyne4) may also be supposed to be unstable intermediates. Calculations have been carried out for benzyne and 3,4-pyridyne by several authors,5-8) but the electron interaction has never explicitly been taken into account in these treatments. In the present paper, calculations on these intermediates and their isomers are performed using a semi-empirical SCF MO method for valence electron systems previously reported on by us.9) Here, however, our procedure is simplified by assuming the zero-differential overlap.[*2]

To estimate the unknown bond lengths of arynes, we utilize such a SCF procedure as has been proposed by Coulson,5) a procedure which makes use of an empirical curve relating the bond order to the bond length.10) In the present treatment, we use the following relation between the bond order and the total electronic energy, E_{AB}, of the AB bond:

$$E_{\mathrm{AB}} = \sum_{r}^{\mathrm{A}} \sum_{s}^{\mathrm{B}} P_{rs}(H_{rs} + F_{rs})$$

where $\sum_{r}^{\mathrm{A}}$ denotes the summation over all the valence AO's which belong to the A atom, and P_{rs}, H_{rs} and F_{rs} are, respectively, the bond order, the core-resonance integral, and Fock's operator between the rth and the sth AO's. The curve is obtained by plotting the E_{AB} values *vs.* the observed bond lengths, R_{AB}, for typical molecules (for example, C_2H_6, C_2H_4, C_6H_6, C_2H_2, *etc.* as to the carbon-carbon bonds). The iteration is repeated until a self-consistency between the initial R_{AB} and that graphically-obtained.

The bond lengths after iteration for the carbon-carbon "triple" bond, presumed to be so at the beginning of the calculations, are as follows (in Å units): 1.29 for benzyne, 3,4-pyridyne, and 2,3-pyridyne; 1.31 for 4,5-pyrimidyne; 1.26 for 2,3-thiophyne and 1.33 for 3,4-thiophyne. These bonds are probably triple bonds in view of their short lengths and large π and π' bond orders. Calculation shows further that the highest occupied (HO) and the lowest vacant (LV) molecular orbitals of arynes may be approximately described as linear combinations of nonbonding sp^2-type hybrids11) of the carbon atoms in the C≡C bond.

TABLE 1. THE CALCULATED LOWEST TRANSITION ENERGIES (σ-σ^*) OF ARYNES (eV)

	State	Singlet	Triplet
Benzyne	B_2	3.73	1.65
3,4-Pyridyne	A′	3.44	1.82
2,3-Pyridyne	A′	3.13	1.60
4,5-Pyrimidyne	A′	2.56	1.46
2,3-Thiophyne	A′	2.80	0.85
3,4-Thiophyne	B_2	2.91	0.86

The calculated lowest transitions are the σ-σ^* type transitions between HO and LV levels mentioned above; the transition energies are presented in Table 1. In Table 1, it may be seen that the lowest triplet states of such arynes as thiophynes lie very close to the ground states. The calculated energies of n-π^* type transitions (4.20 eV for the pyridine $^1B_1$ state, 5.02 eV for the 3,4-pyridyne $^1A''$ state, and 5.95 eV for the 2,3-pyridyne $^1A''$ state) indicate that there exist blue shifts of the bands, taking pyridine as the basis. The larger shift in 2,3-pyridyne than in 3,4-pyridyne may be due to the stronger interaction between the lone pair on the nitrogen atom and the nonbonding sp^2-type hybrids on the carbon atoms. Full details will be published in the near future.

[*1] This may also be called 3,4-dehydropyridine.

[*2] Full details of the present treatment will be published in the near future.

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