

# SEMIQUANTITATIVE EVALUATION OF RESONANCE INTEGRAL AND OVERLAP INTEGRAL FOR C-N BOND IN S-TRIAZINE

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A complete theoretical computation has been made on benzene molecule according to MO method by Mayer and Sklar (1938). The only empirical value used by them was 1.40 Å for the C-C bond length. In the present paper a semi-empirical method has been used, i.e. the theoretical calculation has been combined with spectroscopic data in evaluating the resonance integral for C-N bond in S-triazine (Fig. 1). The method is essentially the same as the one used by Mulliken (1948) for barozol. Calculations on benzene are given here side by side in order to show the correspondence between the two molecules and the applicability of similarity transformation.

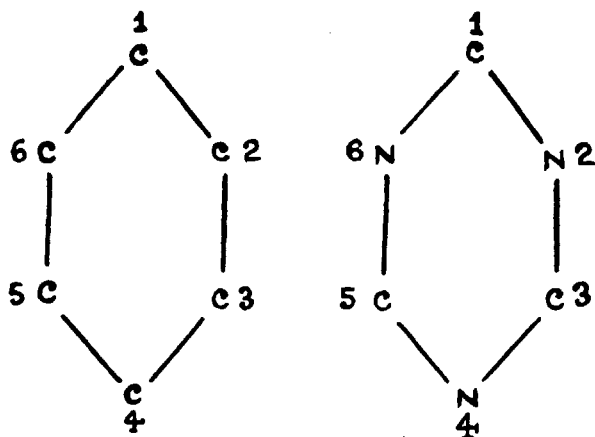


FIG. 1. Benzene and S-triazine

Neglecting non-neighbouring atom interactions we may write the secular determinants for the six approximate MOs as

$$\begin{vmatrix} A & 1 & 0 & 0 & 0 & 1 \\ 1 & A & 1 & 0 & 0 & 0 \\ 0 & 1 & A & 1 & 0 & 0 \\ 0 & 0 & 1 & A & 1 & 0 \\ 0 & 0 & 0 & 1 & A & 1 \\ 1 & 0 & 0 & 0 & 1 & A \end{vmatrix} = 0 \text{ (benzene)}$$

$$\begin{vmatrix} A' & 1 & 0 & 0 & 0 & 1 \\ 1 & A' & 1 & 0 & 0 & 0 \\ 0 & 1 & A' & 1 & 0 & 0 \\ 0 & 0 & 1 & A' & 0 & 0 \\ 0 & 0 & 0 & 1 & A' & 0 \\ 1 & 0 & 0 & 0 & 1 & A' \end{vmatrix} = 0 \text{ (S-triazine)}$$

$$\text{where } A = \frac{\alpha - E}{\gamma - ES}, \quad A' = \frac{\alpha - E}{\gamma^* - ES^*}, \quad A'' = \frac{\alpha^1 - E}{\gamma^* - ES^*}$$

$$\alpha = \int \bar{\Psi}_c^1 H \Psi_c^1 d\tau, \quad \alpha^1 = \int \bar{\Psi}_N^2 H^* \Psi_N^2 d\tau$$

$$\gamma = \int \bar{\Psi}_c^1 H \Psi_c^2 d\tau, \quad \gamma^* = \int \bar{\Psi}_c^1 H^* \Psi_N^2 d\tau$$

$$S = \int \bar{\Psi}_c^1 \Psi_c^2 d\tau \quad \text{and} \quad S^* = \int \bar{\Psi}_c^1 \Psi_N^2 d\tau.$$

The  $\Psi$ 's are atomic  $2p_x$  orbitals, the subscripts refer to the kind of atom and the superscripts to the location in the ring.  $H$  and  $H^*$  are the one electron Hartree field Hamiltonian operator for benzene and S-triazine respectively.

Substituting

$$\alpha - E = -X$$

$$\gamma - \alpha S = \beta$$

$$\gamma^* - \alpha S^* = \beta^*$$

and

$$\alpha^1 - \alpha = \delta$$

we get as a first approximation

$$A = \frac{-X}{\beta - SX}, \quad A' = \frac{-X}{\beta^* - XS^*} \quad \text{and} \quad A'' = \frac{\delta - X}{\beta^* - XS^*}$$

where  $\alpha$ ,  $\gamma$  and  $\beta$  are known to be negative quantities. (The  $\alpha$ 's are electronegativity parameter.) By a suitable similarity transformation the secular determinants can be reduced to the forms:

$$\begin{vmatrix} A & 2 & 0 & 0 & 0 & 0 \\ 2 & A & 0 & 0 & 0 & 0 \\ 0 & 0 & A & 1 & 0 & 0 \\ 0 & 0 & 1 & A & 0 & 0 \\ 0 & 0 & 0 & 0 & A & 1 \\ 0 & 0 & 0 & 0 & 1 & A \end{vmatrix} = 0 \text{ (benzene)} \quad \begin{vmatrix} A' & 2 & 0 & 0 & 0 & 0 \\ 2 & A' & 0 & 0 & 0 & 0 \\ 0 & 0 & A' & 1 & 0 & 0 \\ 0 & 0 & 1 & A' & 0 & 0 \\ 0 & 0 & 0 & 0 & A' & 1 \\ 0 & 0 & 0 & 0 & 1 & A'' \end{vmatrix} = 0 \text{ (S-triazine)}$$

The molecular orbitals corresponding to the roots  $A = -2$  and  $A = -1$  (twice) in benzene and the corresponding orbitals in S-triazine are each occupied in the ground state by two electrons. The average height above the ground state of the first excited state, corresponding in benzene to the excitation of one electron from one of the  $A = -1$  orbitals to one of the  $A = +1$  orbitals is given by the difference ( $X_2 - X_1$ ), of the two roots of

$$A^2 - 1 = 0, \text{ i.e. of } X^2 - (\beta - SX)^2 = 0$$

namely,

$$X_2 - X_1 = -2\beta / (1 - S^2) \text{ for benzene,}$$

and for S-triazine, of

$$A'A'' - 1 = 0, \text{ i.e. } \frac{-X}{(\beta^* - XS^*)} \cdot \frac{\delta - X}{(\beta^* - XS^*)} - 1 = 0$$

or

$$X^2(1 - S^*) + X(2S^*\beta^* - \delta) - \beta^{*2} = 0$$

namely,

$$X_2 - X_1 = -\frac{\beta^*(4+d^2-4dS^*)^{\frac{1}{2}}}{1-S^*}$$

where  $d = \frac{\delta}{\beta^*}$ .

The overlap integral  $S$  and  $S^*$  can easily be evaluated if we use Slater's (1930)  $2p_\pi$  orbitals. The results are

$$S = \left(1 + x + \frac{2}{3}x^2 + \frac{1}{15}x^3\right)e^{-x}$$

for like atoms, and

$$S^* = \left\{ \frac{(ab)^{\frac{1}{2}}}{\frac{1}{2}(a+b)} \right\} \left\{ \frac{1}{\eta^2} \right\} \left\{ \cosh x\eta + \frac{1}{\eta} \sinh x\eta + 3 \left(1 - \frac{1}{\eta^2}\right) \frac{1+x}{x^2} \left( \cosh x\eta - \frac{1}{x\eta} \sinh x\eta \right) \right\} e^{-x}$$

for unlike atoms, where

$$X = Z'R n^*, \text{ for like atoms,} \\ = \frac{1}{2}(a+b) R, \text{ for unlike atoms,}$$

$$a = Z'n^*, b = Z''n^*,$$

$$Z' = \text{effective nuclear charge on carbon} = 3.25,$$

$$Z'' = \text{effective nuclear charge on nitrogen} = 3.90,$$

$$n^* = \text{effective quantum number,}$$

$$= 2 \text{ for } 2p_\pi \text{ orbitals,}$$

$$\eta = \frac{(a-b)}{(a+b)} \text{ (nuclear asymmetry)}$$

and  $R$  = internuclear distance in atomic unit. (Atomic unit of distance is 0.528 Å.)

The actual internuclear distance was taken as 1.41 Å for both C-C and C-N. With these values we get  $S = 0.25$  and  $S^* = 0.235$  and the mean energies from the ground state to the first excited state

$$\text{benzene: } E_2 - E_1 = -2.31\beta,$$

$$\text{S-triazine: } E_2 - E_1 = 1.31\beta^*(4+d^2-0.96d)^{\frac{1}{2}}.$$

The first excited state in benzene is 4.9 eV above the ground state; with this value we get  $\beta$  (spec.), the spectroscopically determined  $\beta$  as

$$\beta_{\text{spec.}} = -4.9/2.13 = -2.30 \text{ eV.}$$

For S-triazine, first excited state is 5.29 eV above ground state (Halverson and Hirst, 1951). So

$$\beta_{\text{spec.}} = \frac{5.29 \times .76}{2} = -2.01 \text{ eV}$$

if  $d = 1$ . This gives  $\delta = -2.01$  eV about 0.3 eV lower than that calculated by Mulliken for nitrogen in borazol.

It may be observed that the values of resonance integral and overlap integral for C-N bond is slightly less than those for C-C bond.

Calculation was not extended to other excited states of S-triazine, since only one absorption band has been experimentally detected for this compound.

### SUMMARY

Theoretical MO calculation has been combined with the spectroscopic data in calculating the overlap integral and resonance integral for C-N bond in S-triazine. The results are 0.235 and -2.01 eV, respectively and slightly lower than C-C bond.

### REFERENCES

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