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# CALCULATION OF HEAT OF FORMATION :- MOLECULAR CONNECTIVITY AND IOC-$\omega$ TECHNIQUE, A COMPARATIVE STUDY

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Abstract - The connectivity index has been used to evaluate the $\pi$-bond energy of alternant and non-alternant hydrocarbons. A new varient of IOC-$\omega$ technique has also been used for the evaluation of $\pi$-bond energy. These methods have now been used to evaluate heats of formation for both types of molecules. A comparative study reveals that the connectivity index based values are generally in better agreement with the experimental values than those obtained with the proposed new varient of the IOC-$\omega$ technique.

## MOLECULAR CONNECTIVITY

Randic's molecular connectivity index represents the degree of branching or connectivity in a molecule and is derived from the vertex degrees or connectivity in the molecule[1-3]. Kier et al. have shown that the connecvity index can be correlated with several physicochemical and biological properties of the molecules[3]. The index $\chi$ has several versions. The simplest, as well as the extended versions ( ${}^{m}\chi$) are calculated from a hydrogen-suppressed graph of molecule. The simplest version, designated as ${}^{1}\chi$ and known as first-order term in $\chi$, is computed by formula :[1-3]

$${}^{1}\chi = \Sigma(\delta_i \delta_j)^{-\frac{1}{2}} \quad .... \quad (1)$$

where the sum is over all connections or edges in the hydrogen-suppressed graph and $\delta_i$ and $\delta_j$ are numbers assigned to each atom reflecting the number of atoms adjacent (connected) to atoms i and j. The nature of the atom is not considered in the calculation.

To account for the nature and unsaturation of the bonds in $\chi$, Kier and Hall[3,4] proposed the valence molecular connectivity ( $\chi^v$) where the atom connectivity is defined as

$$\delta_i^v = Z_i^v - h_i \quad .... \quad (2)$$

in which $Z_i^v$ represents the number of valence electrons of the atom and $h_i$ is the number of hydrogen atoms attached to it. Thus the use of $\delta^v$ permits the calculation of valence term of first order ${}^{1}\chi^v$ by expression -

$${}^{1}\chi^v = \Sigma(\delta_i^v \delta_j^v)^{-\frac{1}{2}} \quad ..... \quad (3)$$

Combining the equations (6) and (7) with (10) we get the following expression for the total $\pi$-electronic energy

$$E_{\pi} = \sum_r q_r\alpha - \omega s \sum_r \sum_{r\neq j} P_{rj} + 2C \sum_{r<s}\sum \frac{P_{rs}}{(1.512-0.174\ P_{rs})^6} \quad \ldots(11)$$

Now consider the energy liberated when 'n' carbon atoms with p-electrons combine to form $\pi$-bonds i.e. energy $E_{\pi b}$. The $\pi$-electronic energy of a molecule is given by the algebraic sum of the energy of electrons in p-orbitals of widely separated carbon atoms and the $\pi$-bond energy ($E_{\pi b}$). The former may be equated to $\sum q_r\alpha$ . Hence the remaining terms give $\pi$-bond energy. For alternant hydrocarbons we have

$$E_{\pi b} = -\omega s \sum_r \sum_{r\neq j} P_{rj} + 2C \sum_{r<s}\sum \frac{P_{rs}}{(1.512-0.174\ P_{rs})^6} \quad \ldots (12)$$

## $\pi$-BOND ENERGY OF NON-ALTERNANT HYDROCARBONS

However, for non-alternant hydrocarbons the expression for $E_{\pi}$ assumes the following form :

$$E_{\pi} = \sum q_r\alpha - \omega s \sum_r \sum_{r\neq j} q_r P_{rj} + 2C \sum_{r<s}\sum \frac{P_{rs}}{(1.512-0.174\ P_{rs})^6} + \omega\sum_r q_r\,(1-q_r) \quad \ldots(13)$$

and hence

$$E_{\pi b} = -\omega s \sum_r \sum_{r\neq j} q_r P_{rj} + 2C \sum_{r<s}\sum \frac{P_{rs}}{(1.512-0.174\ P_{rs})^6} + \omega\sum_r q_r\,(1-q_r) \quad \ldots(14)$$

## CALCULATION OF HEAT OF FORMATION OF ALTERNANT AND NON-ALTERNANT HYDROCARBONS

The heat of formation of a molecule in its equilibrium configuration is the additive sum of the bond energies. The total bond energy of a molecules is given by the sum of the total $\sigma$-bond energy, $E_{\sigma b}$, and the total $\pi$-bond energy $E_{\pi b}$. The following expression provides a simple route to calculate heats of formation of hydrocarbons.

$$\Delta H_f = E_{\sigma b} + E_{\pi b} \quad \ldots(15)$$

If $E_{C-C}$ and $E_{C-H}$ be the bond energies of C-C and C-H bonds respectively, the expression for $E_{\sigma b}$ is

$$E_{\sigma b} = N_C E_{C-C} + N_H E_{C-H} \quad \ldots(16)$$

therefore,

$$\Delta H_f = N_C E_{C-C} + N_H E_{C-H} + E_{\pi b} \quad \ldots(17)$$

where $N_C$ and $N_H$ are numbers of C-C and C-H bonds respectively. By using expression (17) along with equation (4), (5), (12) and (14) one can evaluate the heat of formation of alternant and non-alternant hydrocarbons.

## PARAMETERS USED

For calculating $\pi$-bond energy for alternant hydrocarbons with the help of equation (12) $\omega$ has been assigned a value 2.79152, S has been taken as 0.25 and C has been taken as 9.875, whereas for non-alternant hydrocarbons using equation (14) the values of $\omega$, S and C are 1.4, 0.75 and 11.637 respectively.

For calculating heat of formation with equation (17) the value of $E_{C-C}$ and $E_{C-H}$ have been assigned as 3.80 eV and 4.43 eV respectively as proposed by Dewar and Gleicher[10].

The details of calculations of this term and other higher terms in $\chi$ can be found in Ref.3.

The electronic interaction depends upon the bonding of atoms in a molecule, hence it becomes obvious that the binding energy of the electron must be in some way related with $\chi$ .

In this communication it is proposed that the $\pi$-bond energy can be evaluated on the basis of connectivity index. For alternant hydrocarbons the following equation has been used :-

$$E_{\pi b} = 3.9298\,{}^{1}\chi^{v} + 0.0523 \quad \ldots\ldots \quad (4)$$

and for non-alternant hydrocarbons

$$E_{\pi b} = 4.3279\,{}^{1}\chi^{v} - 1.7666 \quad \ldots\ldots \quad (5)$$

The correlations can be used to predict the $\pi$-bond energy of conjugated systems.

### IOC -$\omega$ TECHNIQUE

Gupta and Krishna[5–8] in a series of papers have proposed a remarkable improvement over the $\omega$-technique by including the so far neglected overlap charge. According to Harris[9], if overlap is included and the net charge on atom r is taken as that resulting when all overlap charges are divided equally among the atoms involved, one obtains:

$$H_{rr} = \alpha + \omega \left[1 - \tfrac{1}{2} \sum_{j} (P_{rj}S_{rj} + P_{jr}S_{jr})\right] \quad \ldots\ldots \quad (6)$$

In this communication for $H_{rs}$ we have used

$$H_{rs} = C/(1.512 - 0.174\, P_{rs})^{6} \quad \ldots\ldots \quad (7)$$

where 'C' is some arbitrary constant.

### $\pi$- BOND ENERGIES OF ALTERNANT HYDROCARBONS

The total $\pi$-bond energy, $E_{\pi b}$ of a molecule is defined as the energy required when 'n' isolated atoms each with a $\pi$-electron combine to form $\pi$-bonds. In the SCF-MO theory this $\pi$ -bond energy is given by

$$E_{\pi b} = \text{(Total molecular orbital energy)} - \text{(total internal electronic energy)} - \text{(Total energy of } \pi\text{-electrons in widely separated carbon atoms)} \quad \ldots\ldots \quad (8)$$

(Since the total molecular orbital energy includes twice of the total interelectronic repulsion). If the molecule is neutral and the atoms in it are more or less neutral, the coulomb repulsion of the cores of atoms should be more or less balanced by the coulomb repulsion of the electrons attached to those cores. Since in the ground state the molecules as well as the atoms are supposed to be neutral, the total $\pi$-bond energy may be taken as

$$E_{\pi b} = \text{(Total molecular orbital energy)} - \text{(Total energy of } \pi\text{-electrons in widely separated carbon atoms)} \quad \ldots\ldots \quad (9)$$

In molecular orbital theory, the $\pi$-electronic energy of a molecule is given by

$$E_{\pi} = \text{Total molecular orbital energy}$$
$$= \sum_{r} \sum_{s} P_{rs} H_{rs} \quad \ldots\ldots \quad (10)$$

Table 1. Calculated and observed heat of formation of alternant hydrocarbons

| Compounds | Value of Chi $^1\chi^v$ | $\pi$-Bond Energy ($E_{\pi b}$) (in eV) | | Heat of formation ($H_f$) with equation (17) in (eV) | | Experimental values of heat of formation (eV) |
|---|---|---|---|---|---|---|
| | | Equation (12) (IOC-$\omega$ Technique) | Equation (4)(connectivity index) | Using $E_{\pi b}$ obtained through equation (12)(IOC-$\omega$ technique) | Using $E_{\pi b}$ obtained through equation (4)(connectivity index) | |
| Benzene | 2.000 | 8.107 | 7.909 | 57.487 | 57.289 | 57.16 |
| Naphthalene | 3.405 | 13.193 | 13.429 | 90.433 | 90.669 | 90.61 |
| Anthracene | 4.810 | 18.132 | 18.949 | 123.232 | 124.049 | 123.93 |
| Stillbene | 4.732 | 18.277 | 18.643 | 128.437 | 128.803 | 128.48 |
| Pyrene | 5.560 | 20.906 | 21.896 | 137.406 | 138.396 | 138.88 |
| Naphthacene | 6.215 | 23.166 | 24.469 | 156.126 | 157.429 | 157.56 |
| Triphenylene | 6.232 | 25.659 | 24.536 | 158.619 | 157.496 | 157.76 |
| Perylene | 6.976 | 26.061 | 27.456 | 170.421 | 171.819 | 172.04 |
| Picene | 7.637 | 28.821 | 30.056 | 189.641 | 190.876 | - |
| Coronene | 8.464 | 31.581 | 33.305 | 198.741 | 200.465 | - |
| Average deviation | | | | 0.828 | 0.216 | |

Table 2. Calculated and observed heat of formation of non-alternant hydrocarbons

| Compounds | Value of Chi $^1\chi^v$ | $\pi$-bond energy ($E_{\pi b}$) (in eV) | | Heat of formation with eq.(17)($H_f$) (in eV) | | Experimental values of heat of formation |
|---|---|---|---|---|---|---|
| | | Equation (14) (IOC-$\omega$ technique) | Equation (5)(connectivity index) | Using $E_{\pi b}$ obtained through equation (14)(IOC-$\omega$ technique) | Using $E_{\pi b}$ obtained through equation (5) (connectivity index) | |
| Methylene cyclopropene | 1.264 | 5.796 | 3.703 | 38.716 | 36.623 | - |
| Fulvene | 1.931 | 8.821 | 6.590 | 58.201 | 55.970 | - |
| Pentalene | 2.738 | 11.400 | 10.083 | 72.180 | 70.863 | - |
| 6-Vinyl-fulvene | 2.608 | 11.969 | 9.520 | 77.809 | 75.360 | - |
| Azulene | 3.405 | 15.400 | 12.969 | 92.640 | 90.209 | 89.19 |
| Sesqui-fulvalene | 4.072 | 18.331 | 15.856 | 112.031 | 109.556 | - |
| Acenaph-thylene | 4.149 | 19.573 | 16.189 | 108.213 | 104.829 | 104.32 |
| Hepta-fulvalene | 4.738 | 21.385 | 18.738 | 131.545 | 128.898 | - |
| Hepta-fulvadiene | 5.399 | 24.347 | 21.599 | 150.967 | 148.219 | - |
| Fluoranthene | 5.565 | 25.956 | 22.3181 | 142.454 | 138.818 | 138.11 |
| Average deviation | | | | 3.895 | 0.745 | |

## RESULTS AND DISCUSSIONS

Table (1) lists the values of $\pi$-bond energy for alternant hydrocarbons as calculated on the basis of equation (4) and equation (12), also listed are the heat of formation using these values.

Table (2) contains the values of $\pi$-bond energy for non-alternant hydrocarbons as calculated on the basis of equation (5) and (14) and also listed are the values of heat of formation usingthese values.

On a comparison of the heat of formation values in table(1)it seems that the values obtained on the basis of connectivity index (Average deviation 0.216)are generally in better agreement with the experimental values as compared with those obtained on the basis of the proposed new varient of IOC-$\omega$ technique (Average deviation 0.828). In table 2 also the Average deviation for connectivity method (0.745) is found to be much better than that for IOC-$\omega$ technique (3.895). It may be concluded that the connectivity index can be successfully used as a parameter for such calculations.

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