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The Relationship of π-Binding Energy with Molecular Connectivity in Hydrocarbons

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Synopsis. Hückel's π-binding energy, E_π, in hydrocarbons is found to be parallel to Kier's molecular connectivity index, χ. In either class of hydrocarbons, alternant or non-alternant, the regression analysis reveals a highly significant linear correlation between E_π and ${}^1\chi^v$ (the first order valence connectivity index).

The molecular connectivity index, χ, signifies the degree of branching or connectivity in a molecule and is derived from the numerical extent of branching or connectivity in the molecular skeleton.[1-3] Kier *et al.* have shown that this index can be correlated with several physicochemical and biological properties of the molecules.[3] The χ has several versions. The simplest as well as extended versions in it (${}^m\chi$) all are calculated from a hydrogen suppressed graph of the molecule. The simplest version designated as ${}^1\chi$ and known as first-order term in χ is computed by[1-3]

$$ {}^1\chi = \sum (\delta_i \delta_j)^{-1/2} \qquad (1) $$

where the sum is over all connections or edges in the hydrogen suppressed graphs, and δ_i and δ_j are numbers assigned to each atom reflecting the number of atoms adjacent or connected to atoms i and j, which are formally bonded. The nature of the atoms is not considered in the calculation.

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

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

in which Z_i^v represents the number of valence electrons of atom i, and h_i the number of hydrogen atoms attached to it. Thus the use of δ^v permits the calculation of valence χ term of first-order, ${}^1\chi^v$, by the expres sion:

$$ {}^1\chi^v = \sum (\delta_i^v \delta_j^v)^{-1/2}. \qquad (3) $$

The details of calculation of this term and other higher terms in χ can be seen in Ref. 3.

The electronic interaction depends upon the specific orientation of atoms in a molecule, hence it becomes obvious that the binding energy of electrons must be in some way related with χ.

Using Eqs. 2 and 3, the ${}^1\chi^v$ values are calculated for some alternant and non-alternant hydrocarbons and listed in Tables 1 and 2 respectively. Hückel's π-binding energy values, E_π, are taken from the literature.[5] A plot of E_π *versus* ${}^1\chi^v$ is shown, for alternant hydrocarbons, in Fig 1, and for non-alternant hydrocarbons, in Fig 2. A straight line is obtained in both the cases. The level of significance of this linear correlation between E_π and ${}^1\chi^v$ in two cases is shown by Eqs. 4 and 5 respectively.

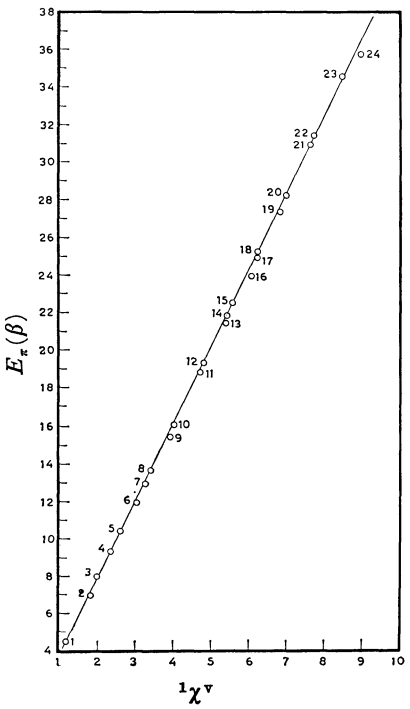

Fig. 1. A plot of E *versus* χ in alternant hydrocarbons. Numbers refer to compounds in Table 1.

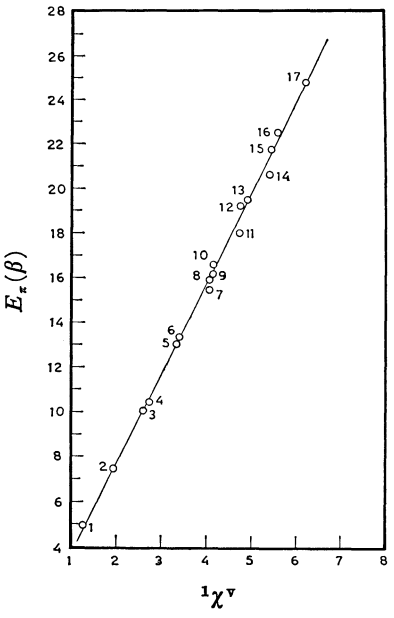

Fig. 2. A plot of E *versus* χ in non-alternant hydrocarbons. Numbers refer to compounds in Table 2. To save space compounds 18 and 19 were not shown.

Table 1. E_π and $^1\chi^v$ values for alternant hydrocarbons

Compd No.	Compound	$^1\chi^v$	E_π (β) Hückel	E_π (β) Calcd from Eq. 4
1	1,3-Butadiene	1.150	4.472	4.378
2	1,3,5-Hexatriene	1.817	6.988	7.093
3	Benzene	2.000	8.000	7.837
4	3,4-Dimethylene-1,5-hexadiene	2.351	9.332	9.266
5	Styrene	2.608	10.422	10.312
6	3,4-Divinyl-1,3,5-hexatriene	3.038	11.925	12.062
7	1-Phenyl-1,3-butadiene	3.274	12.932	13.023
8	Naphthalene	3.405	13.683	13.556
9	1-Phenyl-1,3,5-hexatriene	3.941	15.459	15.737
10	1-Vinylnaphthalene	4.019	16.129	16.055
11	Stilbene	4.732	18.878	18.957
12	Anthracene	4.810	19.314	19.274
13	1,4-Diphenyl-1,3-butadiene	5.399	21.401	21.671
14	9-Vinylanthracene	5.429	21.790	21.793
15	Pyrene	5.560	22.505	22.326
16	1,6-Diphenyl-1,3,5-hexatriene	6.065	23.934	24.382
17	Naphthacene	6.215	24.931	24.992
18	Triphenylene	6.232	25.274	25.061
19	Triphenylethylene	6.810	27.270	27.414
20	Perylene	6.976	28.245	28.089
21	Picene	7.637	30.943	30.780
22	Benzo[*ghi*]perylene	7.720	31.425	31.118
23	Coronene	8.464	34.572	34.146
24	Tetraphenylethylene	8.974	35.719	36.221

$$E_\pi = 4.070\,^1\chi^v - 0.302$$
$$n=24,\ r>0.999,\ s=0.229,\ F_{1,22}>20000 \quad (4)$$
$$E_\pi = 4.068\,^1\chi^v - 0.551$$
$$n=19,\ r=0.999,\ s=0.358,\ F_{1,17}=8483. \quad (5)$$

In these two equations, as obtained by regression analysis, the statistical parameters: n (the number of data points), r (the correlation coefficient), s (the standard deviation), and F (the F ratio between the variances of calculated and observed data) exhibit very high level of significance of the correlations. The E_π values reproduced from Eqs. 4 and 5 are found to be in very good agreement with the Hückel ones (Tables 1 and 2).

Now these correlations can be used to predict the binding energy of any conjugated system. The calculation of χ is utterly simple. These correlations suggest that in biochemical studies χ would be very well able to account for the activity that would depend upon the binding energy of the compounds.

Table 2. E_π and $^1\chi^v$ values for non-alternant hydrocarbons

Compd No.	Compound	$^1\chi^v$	E_π (β) Hückel	E_π (β) Calcd from Eq. 5
1	Methylenecyclopropene	1.264	4.962	4.592
2	Fulvene	1.931	7.466	7.305
3	6-Vinylfulvene	2.608	10.052	10.059
4	Pentalene	2.738	10.456	10.588
5	2-Methylene-2*H*-indene	3.336	13.043	13.021
6	Azulene	3.405	13.363	13.302
7	Fulvadiene	4.065	15.468	15.987
8	Sesquifulvene	4.072	15.931	16.015
9	*s*-Indacene	4.143	16.231	16.304
10	Acenaphthylene	4.149	16.619	16.329
11	Heptafulvalene	4.738	18.005	18.725
12	9-Methylenefluorene	4.758	19.224	18.806
13	Cyclopent[*fg*]-acenaphthylene	4.893	19.476	19.356
14	Heptafulvadiene	5.399	20.608	21.414
15	9-Allylidenefluorene	5.435	21.767	21.561
16	Fluoranthene	5.565	22.500	22.089
17	Benzo[4,5]cyclohepta-[1,2,3-*de*]naphthalene	6.220	24.741	24.754
18	9,9′-Bifluorenylidene	9.060	36.525	36.308
19	1,2-Di(9-fluorenylidene)ethane	9.720	39.073	38.993

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