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ENERGY LEVELS OF NON-ALTERNANT HYDROCARBONS.

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In a recent publication (1) we showed that the relationship between the energies of the internal electronic transitions from the highest occupied orbital to the lowest vacant orbital for a series of donor molecules ($h\nu$), and the charge-transfer transitions for the donors with a given acceptor ($h\nu_{CT}$), should be only approximately linear and related as

$$h\nu_{CT} = \frac{x_i}{x_i + x_j} . h\nu + \text{Constant}$$

where x_i and x_j are respectively the calculated energies (in units of β) of the highest occupied and lowest vacant molecular orbitals of the donors. Lepley (2) had previously shown that for alternant hydrocarbons the slope of the $h\nu_{CT}$ versus $h\nu$ relationship is very close to the theoretical value of one-half and that a number of non-alternant hydrocarbons appeared to lie on an almost parallel line.

We suggested as a possible reason for this that in fully conjugated non alternant hydrocarbons containing an acenaphthylene system the ratio $\frac{x_i}{x_i + x_j}$ may approach one-half with increasing annellation in compounds symmetrical with respect to a plane bisecting the 5-membered ring. However, examination of calculated values for this type of molecule shows that this is not so and that there appears to be no general trend in $\frac{x_i}{x_i + x_j}$ values with annellation (table). The inclusion of calculated x_i and x_j values for a range of symmetrical conjugated non alternant hydrocarbons containing only 5- or 6-membered rings, in addition to those compounds shown in the table, results in an average value for $\frac{x_i}{x_i + x_j}$ of 0.63 for those molecules not possessing non-bonding orbitals or unfilled bonding orbitals. If molecules possessing a non-bonding lowest vacant orbital (provided that they do not have a non-bonding highest occupied orbital e.g. biacenaphthylene) are included, this average value increases to become greater than 0.8 . An increase of this value implies a decrease in the energy of the lowest vacant molecular orbital making these molecules easily reducible or even unstable under normal conditions. The parallel between ease of polarographic reduction and x_j values in the case of fluoranthene derivatives has been pointed out by other workers (3). Recent studies of symmetrical indacene-like hydrocarbons containing a seven-membered ring (e.g. cyclohept[f]indene) by Zahradnik et al. (4) indicate that their $\frac{x_i}{x_i + x_j}$ values should be close to one-half and vary only slightly with linear annellation.

In contrast, the values of x_i and x_j for linearly annellated derivatives of cyclopentadiene --- formally non-fully conjugated non alternant hydrocarbons --- do tend to become equally spaced above and below the arbitrary zero with increasing molecular size. Calculated parameters for some of these compounds are shown in the lower part of the table. Calculations on these molecules may be effected either by considering the $-CH_2-$ group as analogous to a single heteroatom, c.f. indole, dibenzofuran etc., (table, method A), or by assuming that the hyperconjugative effect allows the group to be represented as $-\underset{\substack{|\!|\!| \\ X}}{C}-$, (table, method B), (5). The highest occupied and lowest vacant levels have been chosen assuming that the $-CH_2-$ group contributes two electrons to the π-system.

The main difference between values obtained by these two methods of calculation, using the parameters given at the foot of the table, appears to be a marked lowering of the value of x_j as calculated by the latter method. This results in an increase in the value of the carbon-carbon resonance integral β as calculated from the electronic spectra. It is of interest to note that a high value of β (-3.8 ev.) was obtained from the charge-transfer studies with the corresponding heterocycles (1). The inclusion of an auxiliary inductive parameter (5) of -0.2 in method A decreases x_i and increases x_j for the smaller molecules but has only minor effects upon the larger ones, the sum of x_i and x_j being hardly affected in all cases.

Values of x_i and x_j obtained for the larger symmetrical compounds are almost identical with those for the corresponding biaryls and values for the unsymmetrical ones are similar to those for the corresponding 2-phenyl or 2,2'-naphthyl alternant hydrocarbons, c.f. 11H benzo[b]fluorene and 2-phenylnaphthalene (table). It is thus apparent that in the correlation of $h\nu_{CT}$ with $h\nu$ the hydrocarbons must be split up into classes as done by Lepley (2) and proposed by Zahradnik (6), whence the expected correlations are approximately observed within each class of compounds, and should not be simply grouped together as alternants or non alternants in calculating the slope of this plot.

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References.

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(4) R.Zahradnik, J.Michl and J.Kopecky, Coll. Czech. Chem. Comm., 31, 640, (1966).
(5) A.Streitwieser, Molecular Orbital Theory for Organic Chemists, (J.Wiley & Sons Inc., New York, 1961). Chapter 5.
(6) R.Zahradnik and J.Michl, Coll. Czech. Chem. Comm., 30, 515, (1965).

TABLE

Hydrocarbon		x_i	x_j	$\frac{x_i}{x_i + x_j}$
Acenaphthylene[a]		0.637_5	0.285	0.691
Fluoranthene[a]		0.618	0.371	0.625
3,4-Acefluoranthylene[b]		0.494	0.099	0.833
Benzo[m,n,o]fluoranthene[b]		0.618	0.378	0.620
8,9-Benzofluoranthene[b]		0.459	0.400	0.534
Naphtho[2,3-k]fluoranthene[c]		0.342	0.397	0.463
Indeno[1,2,3-f,g]naphthacene[d]		0.372	0.160	0.700
Diindeno[1,2,3-f,g,1,'2',3'-o,p]naphthacene[d]		0.000	0.732	0.000
Indeno[1,2,3-c,d]fluoranthene[d]		0.580	0.186	0.757
Periflanthene[c]		0.432	0.118	0.785
Decacyclene[b]		0.481	0.333	0.591
Cyclohept [f]indene[e]		0.261	0.215	0.548

* * *

Indene	f	0.631	0.783	0.446
	g	0.554	0.847	0.395
	h	0.651	0.648	0.501
Fluorene	f	0.705	0.752	0.484
	g	0.663	0.768	0.463
	h	0.705	0.696	0.503
11H Benzo[b]fluorene	f	0.528	0.566	0.482
	g	0.515	0.576	0.472
12H Dibenzo[b,h]fluorene	f	0.521	0.521	0.500
	g	0.520	0.521	0.500

Hydrocarbon		x_i	x_j	$\frac{x_i}{x_i + x_j}$
13H Indeno[1,2-b]anthracene	f	0.368	0.396	0.481
6H Benzo[b]Naphtho[2,3-h] fluorene	f	0.372	0.391	0.488
	g	0.364	0.396	0.479
7H Dinaphtho[2,3-b,2'3'-h] fluorene	f	0.357	0.360	0.498
	g	0.355	0.361	0.496
Biphenyl		0.705	0.705	0.500
2-Phenylnaphthalene		0.565	0.565	0.500
2,2'-Binaphthyl		0.521	0.521	0.500
2-Phenylanthracene		0.396	0.396	0.500
2-Naphthylanthracene		0.389	0.389	0.500
2,2'-Bianthryl		0.357	0.357	0.500

<u>Footnotes to table</u>:

a C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations", (Pergamon Press, Oxford, 1965).

b A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations", (Pergamon Press, Oxford, 1965).

c P. Hochman, J. Koutecky and R. Zahradnik, Coll. Czech. Chem. Comm. <u>27</u>, 3053, (1962).

d R. Zahradnik, J. Michl and J. Koutecky, ibid. <u>29</u>, 3185, (1964).

e R. Zahradnik and J. Michl, ibid. <u>30</u>, 3550, (1965).

f Method A calculated using $h_X = 2$ $h_{C_\alpha} = 0$ $k_{C_\alpha - X} = 0.7$

g Method A calculated using $h_X = 2$ $h_{C_\alpha} = -0.2$ $k_{C_\alpha - X} = 0.7$

h Method B calculated using $h_C = 0.5$ $h_X = -0.5$ $h_{C_\alpha} = 0$ $k_{C-X} = 3$ $k_{C_\alpha - C} = 1.0$