

RELATIONSHIP BETWEEN QUANTUM-CHEMICAL INDICES OF REACTIVITY OF POLYCYCLIC ALTERNANT HYDROCARBONS

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A relationship is shown between the integral expressions of the indices of chemical reactivity and a method of calculating the localization energies.¹⁹ The atomic localization energies and some other magnitudes for 21 polycyclic hydrocarbons have been calculated or revised. The correlations between various indices of chemical reactivity have been examined and found to be very close. It is shown that the exactly calculated superdelocalizability is equally suited for assessing the reactivity as is the Wheland localization energy. Moreover, the calculation of the energies of the different complexes of an aromatic hydrocarbon with another molecule can be effected by means of equations involving the same functions as those by which the reactivity indices can be expressed. This may be considered as a justification of the successful application of these indices. The characteristic features of the dependences between the experimental data and the indices are discussed.

For estimates of the reactivity of compounds with double bonds, some quantum-chemical magnitudes that follow from various conceptions of the factors determining the reaction rate are usually employed. These reactivity indices are normally calculated using the Hückel approximation of the m.o. l.c.a.o. method. It has been shown that there exist interdependences between these magnitudes.¹⁻⁵ This is understandable because the quantum-chemical reactivity indices can be expressed by integrals in whose integrand there is a single common function.^{6, 7} On the other hand, no theorems have been derived in the literature that would directly substantiate the wide parallelism of predictions made on the basis of various indices. Only some sufficient, but not necessary, conditions have been derived for conformable statements on the order of the reactivities of the positions within one molecule on the basis of various reactivity indices.⁶⁻⁷

In the present work, we have first calculated the atomic localization energies⁸ for a large number of alternant polycyclic aromatic hydrocarbons (table 2). Moreover, we have revised, or calculated, self-polarizabilities,⁹ free valences,^{5, 10-12} reactivity numbers,¹³ superdelocalizabilities, and approximate superdelocalizabilities¹⁴ (cf. ref. (15)-(18)) for these hydrocarbons. The results of the calculations are summarized in table 3. The data given in this table (except the reactivity numbers which were calculated with an accuracy of 0.01) are subject to an error of 0.001 of the respective units.

These extensive calculations of atomic localization energies have been made possible by employing a recently published method¹⁹ which is suitable for calculations by means of an automatic computer. The orbital energies of the residual

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molecule (formed by taking out the $2p_z$ orbital of the attacked carbon atom) are calculated as roots of the equation¹⁹

$$L_{kk}(W) = 0, \quad (1)$$

where^{19, 20}

$$L_{sj}(W) = \sum_{m=1}^N \frac{\bar{c}_{mj}c_{ms}}{W - E_m} = (-1)^{s+j} \frac{\Delta_{js}(W)}{\Delta(W)}. \quad (2)$$

The subscript k denotes the atom taken out of conjugation: c_{ms} is the coefficient for the s th atomic orbital in the m th molecular orbital whose orbital energy is E_m ; N denotes the number of atomic orbitals in the original molecule, and $\Delta(W)$ is the secular determinant of this molecule. $\Delta_{js}(W)$ is a subdeterminant formed by omitting the j th row and the s th column from $\Delta(W)$. The roots of eqn. (1) yield only those orbital energies of the residual molecule which are not equal to any orbital energy of the original molecule.

For alternant hydrocarbons the left side of eqn. (1) can be rearranged to

$$L_{kk}(W) = 2W \sum_{m=1}^{N/2} \frac{|c_{mk}|^2}{W^2 - E_m^2} = WG_k(W). \quad (3)$$

TABLE 1.—REACTIVITY INDICES FOR ALTERNANT EVEN HYDROCARBONS

magnitudes and signs	definition	expression by means of function $G_k(z)^6$
atomic localization energy A	see eqn. (1), (2)	$-\frac{1}{\pi} \int_{-\infty}^{+\infty} \ln[y^2 G_k(iy)] dy$
autopolarizability π_{kk}	$4 \sum_{i=1}^{N/2} \sum_{j=N/2+1}^N \frac{ c_{ik} ^2 c_{jk} ^2}{E_i - E_j}$	$-\frac{1}{\pi} \int_{-\infty}^{+\infty} y^2 [G_k(iy)]^2 dy$
free valence F	$\sqrt{3 - 2 \sum_{j=1}^{N/2} E_j c_{jk} ^2}$	$\sqrt{3 + \frac{1}{\pi} \int_{-\infty}^{+\infty} [1 - y^2 G_k(iy)] dy}$
superdelocalizability S	$2 \sum_{j=1}^{N/2} \frac{ c_{jk} ^2}{E_j}$	$-\frac{1}{\pi} \int_{-\infty}^{+\infty} G_k(iy) dy$
reactivity number A_D	$2 \left \sum_s d_{0s} \right ^2$ *	$\frac{2}{\sqrt{G_k(0)}}$
approximate superdelocalizability S'	$2 \frac{ c_{N/2, k} ^2}{E_{N/2}}$ †	

* d_{0s} denotes the coefficient for the s th atomic orbital in the non-bonding molecular orbital of the residual molecule formed by taking the orbital out of conjugation in the calculation of the localization energy according to Wheland. The summation \sum_s denotes the addition over the orbitals adjacent to this orbital in the parent molecule.⁵

† The numbering of the orbitals has been selected so that the $N/2$ th orbital is the highest bonding orbital.

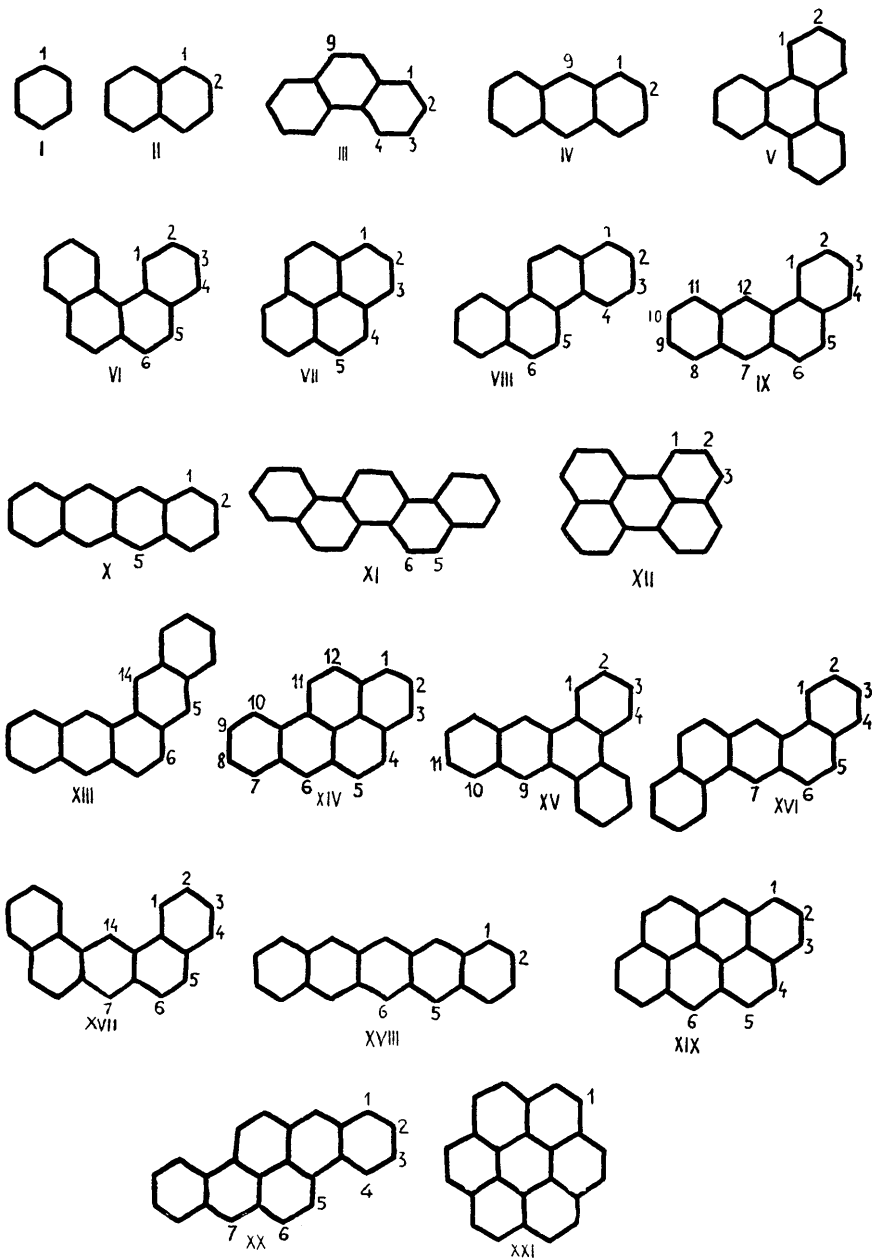
According to eqn. (3), we can define the function

$$G_k(z) = \frac{\Delta_{kk}(z)}{z\Delta(z)}, \quad (4a)$$

or

$$G_k(z) = 2 \sum_{m=1}^{N/2} \frac{|c_{mk}|^2}{E_m^2 - z^2}, \quad (4b)$$

TABLE 2.—LIST OF HYDROCARBONS



where

$$z = W + iy \quad (5)$$

is a complex variable.

Eqn. (4) shows the relationship of the function $G_k(iy)$ appearing in the integrand of the integral expression of the reactivity indices ⁶ to the function $G_k(W)$ in eqn. (3).

TABLE 3.—QUANTUM-CHEMICAL REACTIVITY INDICES OF POLYNUCLEAR AROMATIC HYDROCARBONS *

compound †	$i \ddagger$	A	A_D	F	π_{ii}	S'	S
I. benzene	1	2.536	2.31 ¹³	0.398	0.398	0.333	0.833 ⁵²
II. naphthalene	1	2.299	1.81 ¹³	0.453	0.443	0.585	0.994 ⁵²
	2	2.479	2.12 ¹³	0.404	0.405	0.224	0.873
III. phenanthrene	1	2.320	1.86 ¹³	0.450	0.439	0.382	0.977
	2	2.499	2.18 ¹³	0.403	0.403	0.006	0.860
	3	2.454	2.04 ¹³	0.408	0.407	0.327	0.893
	4	2.367	1.96 ¹³	0.441	0.429	0.179	0.939
	9	2.299	1.80	0.452	0.442	0.569	0.998 ⁵²
IV. anthracene	1	2.230	1.57 ¹³	0.459	0.454	0.467	1.073
	2	2.423	1.89 ¹³	0.408	0.411	0.233	0.922
	9	2.013	1.26 ¹³	0.520	0.526	0.934	1.313 ⁵²
V. triphenylene	1	2.374	2.00	0.439	0.427	0.325	0.928
	2	2.476	2.12 ¹³	0.405	0.406	0.325	0.879
VI. 3, 4-benzphenanthrene	1	2.332	1.86 ¹³	0.445	0.435	0.377	0.969
	2	2.461	2.06	0.407	0.408	0.100	0.887
	3	2.477	2.10 ¹³	0.404	0.405	0.189	0.876
	4	2.312	1.84 ¹³	0.450	0.440	0.316	0.983
	5	2.297	1.79 ¹³	0.451	0.442	0.354	0.999
	6	2.323	1.86 ¹³	0.448	0.438	0.049	0.976
VII. pyrene	1	2.189	1.51 ¹³	0.469	0.467 ⁵¹	0.611	1.116 ⁵²
	2	2.549	2.31 ¹³	0.394	0.395 ⁵¹	0.000	0.829
	4	2.275	1.68 ¹³	0.452	0.444 ⁵¹	0.392	1.025
VIII. chrysene	1	2.303	1.80 ¹³	0.452	0.441 ⁵¹	0.336	0.992
	2	2.492	2.16 ¹³	0.403	0.403 ⁵¹	0.056	0.864
	3	2.448	2.02 ¹³	0.408	0.409 ⁵¹	0.208	0.897
	4	2.349	1.90 ¹³	0.442	0.431 ⁵¹	0.224	0.954
	5	2.348	1.90 ¹³	0.440	0.431 ⁵¹	0.210	0.954
	6	2.248	1.67 ¹³	0.457	0.451 ⁵¹	0.571	1.044 ⁵²
IX. 1, 2-benzanthracene	1	2.370	1.98	0.440	0.429	0.000	0.935
	2	2.436	1.96	0.409	0.410	0.182	0.908
	3	2.488	2.13	0.404	0.404	0.040	0.868
	4	2.316	1.84	0.451	0.439	0.113	0.980
	5	2.258	1.66	0.456	0.448	0.368	1.040
	6	2.260	1.66	0.455	0.447	0.392	1.039
	7	2.050	1.35	0.514	0.514	0.876	1.251 ⁵²
	8	2.246	1.63	0.458	0.452	0.463	1.054
	9	2.446	1.98	0.407	0.409	0.166	0.902
	10	2.430	1.92	0.408	0.410	0.246	0.915
	11	2.258	1.66	0.456	0.449	0.399	1.040
	12	2.102	1.44	0.502	0.496	0.684	1.187
X. tetracene	1	2.200	1.42 ¹³	0.461	0.457	0.382	1.121
	2	2.384	1.69 ¹³	0.410	0.414	0.228	0.961
	5	1.932	1.03	0.530	0.556	0.999	1.505
XI. picene	5	2.253	1.67	0.457	0.451	0.480	1.043
	6	2.337	1.86	0.442	0.432	0.258	0.965
XII. perylene	1	2.203	1.45	0.459	0.458	0.480	1.117
	2	2.510	2.12 ¹³	0.396	0.398	0.075	0.856
	3	2.139	1.33 ¹³	0.473	0.476	0.621	1.195
XIII. pentaphene	5	2.052	1.36 ¹³	0.514	0.512	0.641	1.246
	6	2.232	1.58 ¹³	0.458	0.454	0.512	1.073
	14	2.112	1.47 ¹³	0.501	0.492	0.206	1.169

TABLE 3—*cont.*

compound †	<i>i</i> ‡	<i>A</i>	<i>A</i> _D	<i>F</i>	π_{II}	<i>S'</i>	<i>S</i>
XIV. 3, 4-benzpyrene ^{53, 54}	1	2.152	1.38	0.472 ⁵⁴	0.474	0.623	1.176
	2	2.542	2.27	0.394 ⁵⁴	0.395	0.016	0.834
	3	2.168	1.42	0.470 ⁵⁴	0.470	0.551	1.153
	4	2.242	1.55	0.455 ⁵⁴	0.449	0.406	1.070
	5	2.240	1.55	0.455 ⁵⁴	0.450	0.408	1.070
	6	1.962	1.16	0.529 ⁵⁴	0.547	1.015	1.408
	7	2.232	1.55	0.459 ⁵⁴	0.453	0.387	1.076
	8	2.488	2.12	0.402 ⁵⁴	0.403	0.042	0.869
	9	2.380	1.73	0.413 ⁵⁴	0.416	0.299	0.963
	10	2.336	1.81	0.442 ⁵⁴	0.432	0.166	0.970
	11	2.342	1.81	0.440 ⁵⁴	0.430	0.176	0.967
	12	2.220	1.50	0.458 ⁵⁴	0.455	0.466	1.095
XV. 1, 2 ; 3, 4-dibenz-anthracene	1	2.378	2.00 ¹³	0.440	0.427	0.016	0.928
	2	2.468	2.08 ¹³	0.405	0.406	0.103	0.882
	3	2.468	2.08 ¹³	0.404	0.407	0.082	0.881
	4	2.378	2.00 ¹³	0.439	0.427	0.032	0.928
	9	2.122	1.50 ¹³	0.499	0.489	0.716	1.153
	10	2.264	1.70 ¹³	0.457	0.448	0.457	0.029
XVI. 1, 2 ; 5, 6-dibenz-anthracene	11	2.450	2.00 ¹³	0.407	0.409	0.204	0.899
	1	2.364	1.97 ¹³	0.441	0.427 ⁵¹	0.013	0.935
	2	2.438	1.97 ¹³	0.409	0.409 ⁵¹	0.198	0.906
	3	2.489	2.16 ¹³	0.403	0.403 ⁵¹	0.009	0.865
	4	2.309	1.83 ¹³	0.450	0.439 ⁵¹	0.160	0.982
	5	2.259	1.66 ¹³	0.455	0.449 ⁵¹	0.430	1.040
XVII. 1, 2 ; 7, 8-dibenz-anthracene	6	2.277	1.71 ¹³	0.453	0.445 ⁵¹	0.354	1.021
	7	2.130	1.51 ¹³	0.498	0.487 ⁵¹	0.573	1.146 ⁵²
	1	2.363	1.95 ¹³	0.441	0.428	0.000	0.941
	2	2.443	1.99 ¹³	0.409	0.408	0.163	0.903
	3	2.485	2.13 ¹³	0.403	0.401	0.047	0.869
	4	2.315	1.85 ¹³	0.450	0.436	0.088	0.978
XVIII. pentacene	5	2.268	1.71 ¹³	0.454	0.448	0.284	1.025
	6	2.270	1.70 ¹³	0.454	0.449	0.390	1.029
	7	2.082	1.44 ¹³	0.510	0.502	0.833	1.200
	14	2.176	1.60 ¹³	0.486	0.470	0.526	1.092
	1	2.182	1.30	0.461	0.459	0.321	1.154
	2	2.362	1.54 ¹³	0.411	0.415	0.216	0.991
XIX. anthanthrene	5	1.894	0.88	0.532	0.569	0.964	1.635
	6	1.842	0.80 ¹³	0.540	0.601	1.285	1.794
	1	2.072	1.15	0.480 ⁵⁴	0.494	0.738	1.312
	2	2.538	2.24	0.393 ⁵⁴	0.395	0.022	0.836
	3	2.098	1.20	0.476 ⁵⁴	0.486	0.666	1.273
	4	2.234	1.49	0.454 ⁵⁴	0.450	0.300	1.080
XX. 3, 4 ; 8, 9-di-benzpyrene	5	2.232	1.49	0.455 ⁵⁴	0.450	0.296	1.082
	6	1.928	1.03	0.531 ⁵⁴	0.557	0.972	1.505
	1	2.208	1.45	0.460 ⁵⁴	0.456	0.369	1.109
	2	2.476	2.06	0.403 ⁵⁴	0.404	0.055	0.877
	3	2.358	1.62	0.414 ⁵⁴	0.418	0.285	0.990
	4	2.322	1.73	0.442 ⁵⁴	0.433	0.157	0.985
XXI. coronene	5	2.300	1.64	0.442 ⁵⁴	0.434	0.229	1.009
	6	2.174	1.33	0.462 ⁵⁴	0.463	0.514	1.165
	7	1.910	1.01	0.535 ⁵⁴	0.567	1.070	1.536
	1	2.307	1.80	0.449	0.440	0.419	0.991

* The sources of data are given only where not taken from our own work or from the *Dictionary of Values of Molecular Constants*, vol. II.⁵⁰

† In this work we use the current terms for aromatic hydrocarbons; the numbering of individual positions, however, is consecutive.

‡ The orbital energies of the residual molecule formed by taking out the pertinent p_z orbital from the conjugation are available from the authors.

Table 1 gives the definitions and integral expressions of the reactivity indices. On substitution of the function $G_k(iy)$ of eqn. (4b) into the integral expressions of F , S and π_{kk} , we effect the integration, and obtain the defining equation of these reactivity indices. Such an integration in closed form is not possible for the localization energy, which, however, is simply determined by the real roots of the function $G_k(z)$.

The function $G_k(W)$ occurs also in the equations for the calculation of the orbital energies of molecules formed by attaching further atoms to the original hydrocarbon. For instance, according to the equation,^{21, 22}

$$L_{kk}^I(W) = \frac{\beta_{cx}^2}{W - \alpha_x}, \quad (6)$$

it is possible to calculate the orbital energies of the system formed by connecting the atomic orbital X to the k th orbital of the hydrocarbon I. The orbital X is here characterized by the Coulomb integral α_x and its bond with the hydrocarbon I by the resonance integral β_{cx} . As a further example, we take a molecule which we imagine as being formed by a bond between the k th atom of the hydrocarbon I and the j th atom of the hydrocarbon II. If the resonance integral between these atoms equals the resonance integral of the p_z orbital of the aromatic hydrocarbon we can determine the orbital energy as the roots of the equation^{21, 22}

$$L_{kk}^I(W) \cdot L_{jj}^{II}(W) = 1. \quad (7)$$

The Roman figures in eqn. (6) and (7) indicate the systems for which the given magnitudes are defined.

With regard to the similarity of eqn. (1) and (6), it is not surprising to find a similar parallelism of the localization energies of Wheland⁸ and the energy of a model of the transition complex of Muller, Pickett and Mulliken²³ (cf. ref. (24)-(27).)

The character of the reactivity number^{13, 28} differs somewhat from that of the other indices. This quantity was originally derived as a first approximation of the atomic localization energy by the perturbation method.²⁹ It is known, however, that the perturbation method is justified only when the differences between the individual energy levels of the unperturbed system are higher than the magnitude of the perturbation. This condition is not satisfied in the case under consideration. Nevertheless, it has been found that good agreement of the experimentally determined reactivity and of the reactivity estimates is obtained on the basis of the reactivity number.³⁰⁻³¹ This fact has been explained by the assumption that the neglected perturbations of second order are practically constant.³² According to this concept, a relation of the following form should exist between reactivity number and atomic localization energy:

$$A = aA_D + b, \quad (8)$$

where a , b are constants, the first of which equals unity. Actually, as shown by Pullman,³³ the relation (8) holds approximately, but the constant a differs from unity. The applicability of the reactivity number is therefore not based on the fact that it is an approximate value of the localization energy, but is due to its connection with the function $G_k(z)$: it is inversely proportional to the root of the value of this function when the argument equals zero.⁶

The dependence of free valence, self-polarizability, reactivity number and superdelocalizability on the atomic localization energy is shown in fig. 1-4. Since the atomic localization energy is clearly connected with the activation energy, we have taken it as a basis for the study of correlations between the indices of chemical reactivity.

These dependences of the various indices on the atomic localization energy confirm the known findings of the close correlation of these magnitudes for secondary

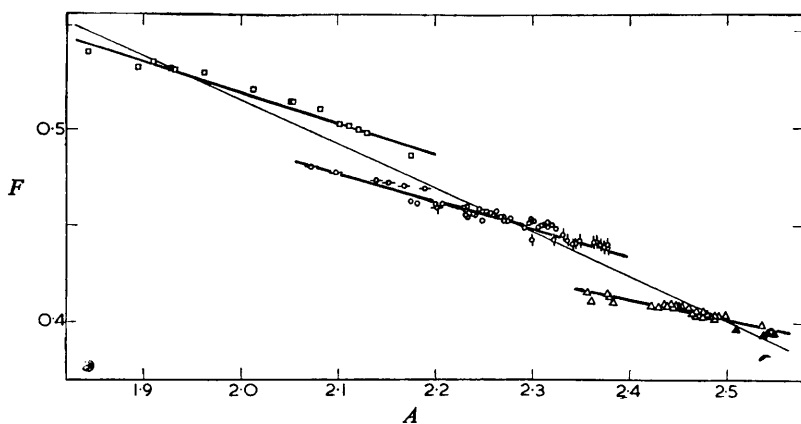


FIG. 1.—Free valence F plotted against atomic localization energy A .
Symbols (class): Δ (0), \circ (1), \square (2); (subclass): \blacktriangle (a), \circ (b), \diamond (c).

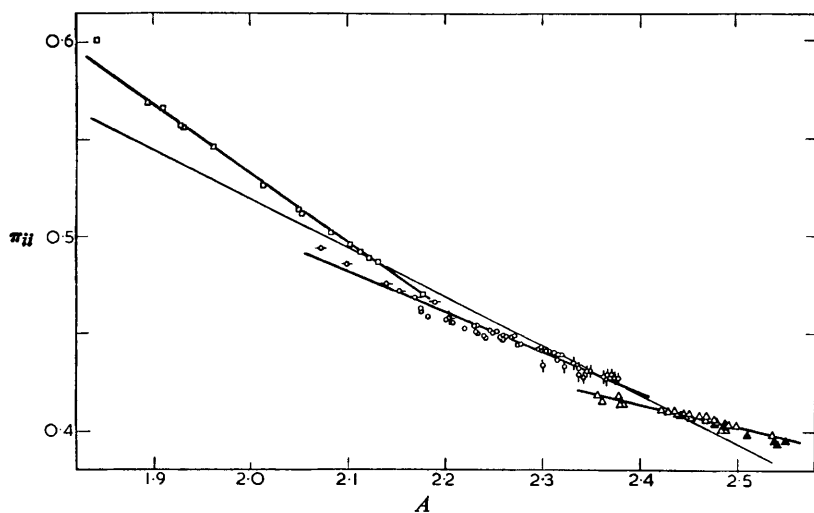


FIG. 2.—Autopolarizability π_{ii} plotted against atomic localization energy A .
Symbols (class): Δ (0), \circ (1), \square (2); (subclass): \blacktriangle (a), \circ (b), \diamond (c).

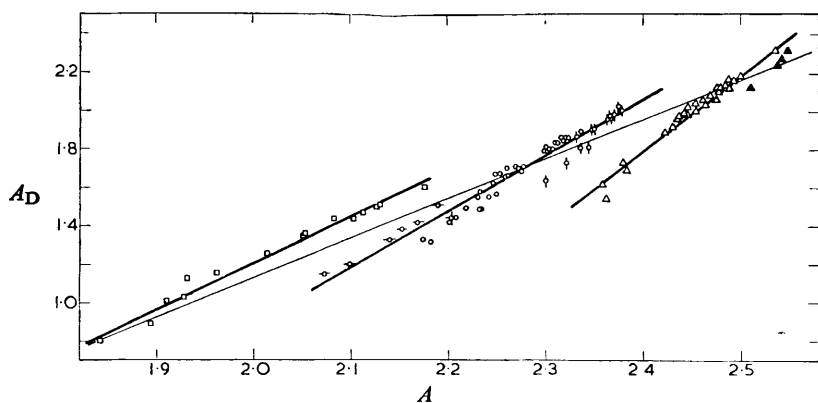


FIG. 3.—Reactivity number A_D plotted against atomic localization energy A .
Symbols (class): Δ (0), \circ (1), \square (2); (subclass): \blacktriangle (a), \circ (b), \diamond (c).

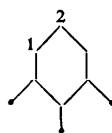
carbon atoms in polynuclear aromatic hydrocarbons. It is known that these empirical dependences may be divided into continuous partial functions for primary, secondary and tertiary positions. It appears, however, that these dependences may be further divided into partial continuous functions for three classes of secondary positions. These positions are characterized by the circumstance that

the considered carbon atom is bound to 0, 1 or 2 tertiary carbon atoms (classes 0, 1, 2). For example, atoms 2, 1 and 9 of anthracene belong, according to this classification, to classes 0, 1 and 2 respectively. Within the individual classes, the correlation is very close and, apart from the superdelocalizability, the dependences can be well represented by straight lines. Only the correlation of the approximate superdelocalizabilities is less close than that of other parameters, and there are, in individual important cases, considerable deviations from the continuous course of this dependence. By a more detailed analysis, however, we find a further characteristic behaviour of the data for carbon atoms, which can be grouped into several sub-classes.

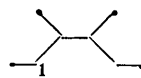
In class 0: (a) position 2 in group (A) (e.g. position 2 in pyrene and in anthanthrene).

In class 1: (b) position 1 in group (A) (e.g. position 1 in pyrene and in anthanthrene).

(c) position 1 in group (B) (e.g. atom 4 in phenanthrene or atom 5 in 3, 4;8, 9-dibenzpyrene).



(A)



(B)

FIG. 4.—Logarithm of superdelocalizability on logarithm of atomic localization energy.

Symbols (class): Δ (0), \circ (1), \square (2).

Analogously, the interdependences of F , π_{kk} and A_D are divided into partial dependences.

For the individual overall and partial dependences, the straight regression lines

$$y - \bar{y} = b_{yx}(x - \bar{x}) \quad (9)$$

were calculated. Tables 4 and 5 present data necessary for the application of eqn. (9), together with the corresponding correlation coefficients.

According to published papers, it may be expected that the use of different indices would lead to different estimates of the place of the maximum reactivity of the hydrocarbon only in exceptional cases. A more general and, from a practical point of view, particularly interesting, question concerns the agreement as to the order of reactivity of the individual positions in one hydrocarbon. It appears that the order of reactivity in all molecules studied is in agreement when it is estimated by means of the indices A , π_{kk} , F and S . The order of magnitude

of A_D agrees with that of A within one molecule, apart from the following exceptions: 1,2-benzanthracene: for A , $1 < 10 < 2$ while for A_D $10 < 2 < 1$; in 3,4-benzpyrene: for A , $10 < 11 < 9$ while for A_D $9 < 10 < 11$; in 3,4;8,9-dibenzpyrene: for A , $5 < 4 < 3$ while for A_D , $3 < 5 < 4$. In the case of approximate superdelocalizabilities (and thus also of frontier electron density) there is no agreement of order for phenanthrene, 3,4-benzphenanthrene, 1,2-benzanthracene, 3,4-benzpyrene, 1,2;3,4-, 1,2;5,6- and 1,2;7,8-dibenzanthracene and 3,4;8,9-dibenzpyrene.

TABLE 4.—AVERAGE VALUE OF INDICES OF CHEMICAL REACTIVITY

magnitude	total	class 0	class 1	class 2
A	2.293	2.464	2.271	2.020
$\log A$	0.3593	0.3915	0.3560	0.3049
A_D	1.73	2.04	1.68	1.26
F	0.4478	0.4047	1.4532	0.5161
π_{ii}	0.4458	0.4059	0.4464	0.5257
$\log S$	0.7095	0.6479	0.7133	0.8222

TABLE 5.—CORRELATION AND REGRESSION COEFFICIENTS

y	A_D				F			
	total	cl. 0	cl. 1	Cl. 2	total	cl. 0	cl. 1	cl. 2
set								
r_{Ay}	0.974	0.982	0.989	0.994	0.979	0.937	0.966	0.981
b_{yA}	2.007	3.857	2.936	2.454	-0.2286	-0.1050	-0.1327	-0.1581
b_{Ay}	0.4726	0.2501	0.3331	0.4029	-4.190	-8.354	-7.037	-6.092
y	π_{ii}				$\log S^*$			
	total	cl. 0	cl. 1	cl. 2	total	cl. 0	cl. 1	cl. 2
set								
r_{Ay}	0.978	0.968	0.985	0.998	0.9936	0.990	0.999 ₈	0.997
b_{yA}	-0.2588	-0.1211	-0.2044	-0.3722	-2.145	-2.261	-2.495	-2.928
b_{Ay}	-3.694	-7.740	-4.750	-2.675	-0.4613	-0.4333	-0.4006	-0.3394

* For superdelocalizability read $\log A$, instead of A .

It is evident that the atomic localization energies and the superdelocalizability are equally useful for estimating the order of reactivity in aromatic alternant hydrocarbons. On the other hand, the approximate superdelocalizability cannot be recommended as a reactivity index. With regard to the non-linear dependence of the superdelocalizability on the atomic localization energy, both these magnitudes cannot be proportional to the activation energy of the reaction (cf. ref. (18)).

The static indices, too, behave similarly to the atomic localization energy, so that the non-crossing rule³⁴ holds for all the hydrocarbons studied. The static indices are considerably less sensitive to differences in the structure of the more remote part of the molecule than are the atomic localization energies or the superdelocalizabilities. The differences between the free valences of different classes are, for instance, very considerable in comparison with the differences within one class. In many cases it was found that the dependences of the reactivity indices on other magnitudes could be divided into partial dependences according to the classes 0, 1 and 2.

In connection with the anomalous behaviour of pyrene and perylene in the inhibition of the auto-oxidation of benzaldehyde, Pullman and Effinger³⁵ noted the dependence of the free valence upon the lowest unoccupied orbital in the hydrocarbon. It appears that the dependence of the free valence, as well as of the atomic localization energy, of the most reactive position of the hydrocarbon on its lowest occupied orbital is divided into partial dependences. The dependences relate to hydrocarbons in which the most reactive position belongs to the class 0,

1 or 2 (cf. fig. 5). The dependence of the localization energy, calculated by the semi-empirical s.c.f. method, upon that in the Hückel approximation may be divided in a similar way^{36, 37} (cf. ref. (38)).

It has been stated that the localization energy in a certain position of the hydrocarbon and the energy of the molecule formed by attaching a group of atoms to the carbon atom in the same position are determined by the roots of

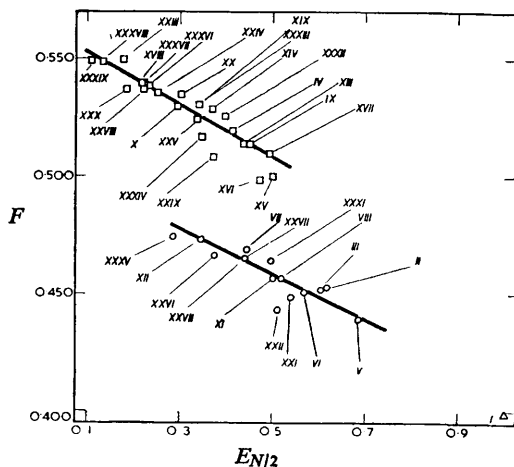


FIG. 5.—Lowest Hückel empty orbital plotted against maximum free valence. The carbon atom of maximum free valence belongs to the class 0 (Δ), 1 (\circ), 2 (\square). The Roman figures up to XXI denote hydrocarbons labelled in table 1. The data for hydrocarbons XXII–XXXIX are from ref. (50)–(53) and private communications: dibenzo [*a, c*] triphenylene (XXII), phenanthro [*1, 10, 9, 8-f; g, h, i, j*] perylene (XXIII), dibenzo [*bc, ef*] coronene (XXIV), ovalene (XXV), tetrabenzo [*bc, gh, kl, pr*] naphthacene (XXVI), 1, 12-benzoperylene (XXVII), tribenzo [*cd, ghi, lm*] perylene (XXVIII), tribenzo [*a, i, l*] pyrene (XXIX), dibenzo [*bc, kl*] coronene (XXX), benzo [*e*] pyrene (XXXI), dibenzo [*a, l*] pyrene (XXXII), dibenzo [*a, i*] pyrene (XXXIII), dibenzo [*b, k*] chrysene (XXXIV), dibenzo [*cd, lm*] perylene (XXXV), violanthrene (XXXVI), isoviolanthrene (XXXVII), heptacene (XXXVIII), octacene (XXXIX).

similar equations. Let us now consider the behaviour of the dependence of the magnitude

$$\Delta\epsilon_{k_{ij}} = \epsilon_{k_{ij}}^{I+II} - \epsilon^I - \epsilon^{II} \quad (10)$$

upon the atomic localization energy. In eqn. (10), $\epsilon_{k_{ij}}^{I+II}$ is the π -electron energy of the system formed by connecting the systems I and II with the corresponding π -electron energies ϵ^I and ϵ^{II} . Fig. 6 illustrates the case in which the group II is a carbon atom or an allyl radical. The dependences are very close and exhibit no noticeable separation into partial dependences. In fig. 7 a similar dependence is plotted for the case where the Coulomb integral as well as the resonance integral of the attached atom equals unity, the highest bonding orbital being occupied by two electrons. Fig. 8 shows a similar dependence when the highest bonding orbital is unoccupied. In the first case, we obtain a close dependence, while in the second case a separation into partial dependences exists depending on which class the carbon atom belongs to and where the attachment is effected.

The dependence of experimentally determined rate constants of substitution reactions upon the localization energies, or the free valence, exhibits considerable splittings into partial dependences for compounds in which the reaction proceeds on atoms of class 0, 1 or 2, e.g., nitration,³⁹ and probably chlorination,⁴⁰ of aromatic hydrocarbons, and inhibitory effect of hydrocarbons on the auto-oxidation of

benzaldehyde.^{41, 42} Similar splittings are found for reactions proceeding at the side-chain of substituted hydrocarbons. The logarithm of the rate constant is correlated with the reactivity index of that carbon atom of the parent hydrocarbon which carries the substituent. This phenomenon was observed in the solvolysis of arylmethyl chlorides⁴³⁻⁴⁵ and aryethyl chlorides,⁴⁶ in the exchange reaction⁴³

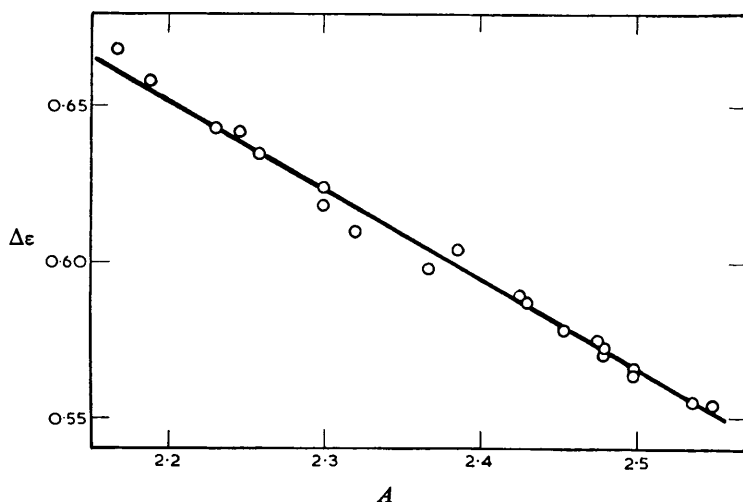


FIG. 6.—Magnitude $\Delta\epsilon_{kj}$ (cf. eqn. (10)) plotted against localization energy of atom k of aromatic hydrocarbon for attachment of allyl radical to atom k .

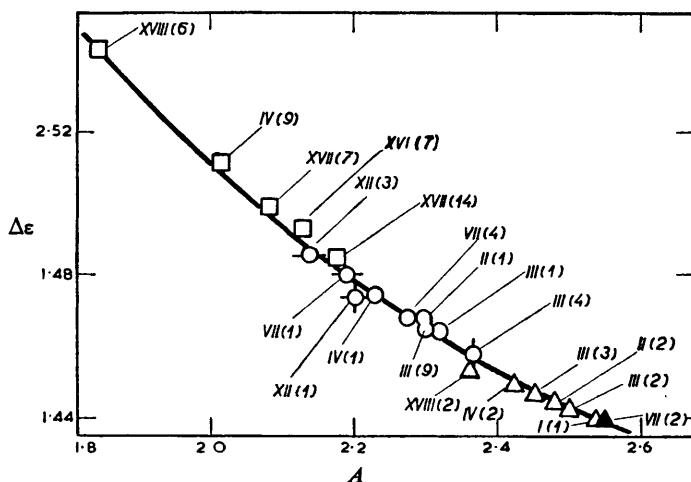


FIG. 7.—Magnitude $\Delta\epsilon_{kj}$ (cf. eqn. (10)) plotted against localization energy of atom k of aromatic hydrocarbon for attachment of an atom having $\alpha_X = 1$, $\beta_{CX} = 1$; highest bonding orbital occupied. Some data taken from ref. (26).

of the halogen in arylmethyl chlorides, and in the alkaline hydrolysis⁴⁷ of esters of carboxylic acids. The cause was in most cases ascribed to the different extent of the effect of steric inhibition at the positions of different classes. On the other hand, Pullman and Effinger³⁵ assume that the logarithm of the rate constant of some reactions must be correlated with the energy of the lowest unoccupied

orbital of the hydrocarbon. No splitting of the dependences was observed in the substitution of hydrocarbon by the methyl⁴⁸ radical nor by the large trichloromethyl⁴⁹ radical.

CONCLUSIONS

(i) The calculation of the energies of the molecular orbitals of most complexes formed by combination of an aromatic hydrocarbon with another molecule by a single bond uses the approximation of the m.o. l.c.a.o. method for ascertaining the roots of the equation in which the properties of the hydrocarbon manifest themselves by means of a single function $G_k(W)$. On this function also depend the commonly employed reactivity indices. It is not excluded that the successful

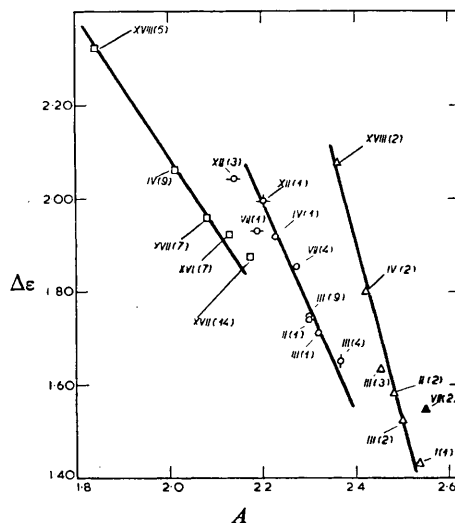


FIG. 8.—Magnitude $\Delta\epsilon_{kj}$ (cf. eqn. (10)) plotted against localization energy of atom k of aromatic hydrocarbon for attachment of an atom having $\alpha_X = 1$, $\beta_{CX} = 1$, highest bonding orbital unoccupied. Some data taken from ref. (26).

use of these indices is due to the fact that the reactivity indices and the differences between the energies of the complexes and of the initial systems behave very similarly when we take as initial system I various hydrocarbons and as initial system II the same molecule representing a model reagent.

(ii) For secondary carbon atoms linked with the same number of tertiary carbon atoms, the mutual correlations between the reactivity indices as well as the correlations between these indices and other quantum-chemical magnitudes are very close. The separation of these dependences into partial dependences according to the classes defined in the present work necessitates caution in interpreting analogous separations of the dependences of the experimental rate constants on the reactivity indices. In principle, there are the following possible explanations:

- effect of steric hindrance;
- correlation with an unsuitable reactivity index;
- the empirical reactivities should for a given mechanism be correlated with another theoretical magnitude characterizing the original hydrocarbon (e.g. affinity to the electron);
- the Hückel approximation is insufficient;
- the empirical magnitudes should be correlated with a magnitude describing the transition complex.

It is probable that simultaneous development of theory and experimental investigation of the reactivities will make possible a decision between these alternatives. Such a study of the separations of the dependences could also aid in ascertaining the mechanism of the reactions. For instance, if assumption (e) were valid, it would be possible to decide between the mechanism S_N2 and the mechanism S_E2 or S_N1 .²⁶

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