A Simple Reactivity Index for Alternant Hydrocarbons

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Several quantum-chemical reactivity indexes for the conjugated system have been proposed in LCAO MO treatment and each of these quantities has been found to explain well the experimental results. One of these indexes is the superdelocalizability, S_r. This is derived from the frontier electron theory[1] and has been proved to be an excellent guide to explain various experimental results of conjugated molecules. In the larger molecules, however, a laborious calculation is required to obtain its value. Therefore, a method to be a good appoximation to S_r, which would make computation considerably easier, may be looked forward to. In this view the authors derive a new reactivity index, $\bar{S}_r$ for alternant hydrocarbons. That is, $\bar{S}_r$ is the ratio of $b_{r,m-1}$ to a_m, where a_m and $b_{r,m-1}$ are the constant terms of expanded secular determinants given by Eq. 4. In this paper, values of $\bar{S}_r$ are compared with exact values of S_r, and also with experiments together with the localization energy.

In spite of its extreme simplicity, $\bar{S}_r$ is a good reactivity index of the alternant hydrocarbon. Accordingly, it is suggested to use this index widely for the purpose of concise explanation of reactivity of large alternant hydrocarbon molecules.

Theoretical

Superdelocalizability, S_r, is given by the following formula[1]

$$S_r=\sum_{j=1}^{N}\frac{(\nu_j-\nu)(c_r{}^j)^2}{\lambda_j} \tag{1}$$

where $c_r{}^j$ is the coefficient of the rth atomic π-orbital in the jth molecular orbital, and λ_j is the energy of the jth molecular orbital in unit of β (the resonance integral of benzene), respectively; ν_j is the number of electrons in the jth molecular orbital, ν is the number of electrons at the pseudo-π orbital in the transition state and stands for 0, 1 and 2, for an electrophilic, radical and nucleophilic reaction, respectively. Also N represents the total number of molecular orbitals.

In our previous paper[2] a function $G_r(y)$ is defined as

$$G_r(y)=\Delta_{rr}(iy)/iy\Delta(iy) \tag{2}$$

where $\Delta(\lambda)$ is the secular determinant for the isolated molecule, and $\Delta_{rr}(\lambda)$ is the (rr) minor of $\Delta(\lambda)$. In Eq. 2 the argument λ is replaced by iy. In alternant hydrocarbons, Eq. 1 is represented, using the function $G_r(y)$, by an integral formula as

$$S_r=\frac{(-\beta)}{\pi}\int_{-\infty}^{\infty}G_r(y)\mathrm{d}y \tag{3}$$

The determinants $\Delta(iy)$ and $\Delta_{rr}(iy)$ are expanded in the forms;

$$\left.\begin{aligned}(-1)^m\Delta(iy)&=y^{2m}+a_1\beta^2y^{2m-2}\\&\quad+a_2\beta^4y^{2m-4}+\cdots\cdots+a_m\beta^{2m}\\(-1)^m\frac{\Delta_{rr}(iy)}{iy}&=y^{2m-2}+b_{r,1}\beta^2y^{2m-4}\\&\quad+b_{r,2}\beta^4y^{2m-6}+\cdots\cdots+b_{r,m-1}\beta^{2m-2}\end{aligned}\right\} \tag{4}$$

It is proved algebraically that

$$\left.\begin{aligned}&a_i>0\quad(i=1,2,\cdots\cdots,m)\\&b_{r,i}>0\quad(i=1,2,\cdots\cdots,m-1)\\&\frac{b_{r,j}}{a_j}\geqq\frac{b_{r,j+1}}{a_{j+1}}\quad(j=0,1,2,\cdots\cdots,m-1)\\&\frac{b_{r,j-1}}{a_j}\leqq\frac{b_{r,j}}{a_{j+1}}\quad(j=0,1,2,\cdots\cdots,m-1)\\&\qquad(b_{r,-1}=0,\ a_0=b_{r,0}=1,\ b_{r,m}=0)\end{aligned}\right\} \tag{5}$$

Considering the conditions of Eq. 5, one can easily show that $G_r(y)$ is positive with respect to all the real values of y. Further, it is clearly seen that $G_r(0)$ is equal to $b_{r,m-1}/a_m\cdot\beta^{-2}$, and that $G_r(y)$ is an even function of y and converges to zero according as y tends to infinite, and $\frac{\mathrm{d}}{\mathrm{d}y}G_r(y)$ is negative with respect to all the positive values of y. The curve of $G_r(y)$ plotted against y can be qualitatively shown in Fig. 1. The integration of curve I in the range $-\infty<y<+\infty$ gives the value of S_r exactly. Here, we adopt an approximation. In place of curve I, the integration of curve II is carried out. Its value is equal to $G_r(0)$ between $-\pi(-\beta)/2$ and $+\pi(-\beta)/2$ and is zero for $|y|>\pi(-\beta)/2$. If we designate the

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[1] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, 27, 1247 (1957).

[2] K. Fukui, T. Yonezawa and C. Nagata, ibid. 26, 831 (1957).

Table I. The values of S_r and $\overline{S}_r$ in several alternant hydrocarbons in comparison with experiment

Compound	Position	S_r	$\overline{S}_r$
Benzene		0.833	0.750
Naphthalene	1*	0.994	1.222
	2	0.873	0.889
	9	0.703	0.555
Anthracene	9*	1.314	2.500
	1	1.073	1.625
	2	0.921	1.125
Naphthacene	12*	1.505	3.800
	1	1.121	2.000
	2	0.961	1.400
Pentacene	13*	1.794	6.250
	14	1.634	5.111
	1	1.154	2.361
	2	0.991	1.694
Phenanthrene	10*	0.997	1.240
	1	0.978	1.160
	4	0.940	1.140
	3	0.892	0.960
	2	0.859	0.840
Pyrene	3*	1.150	1.444
	2	1.026	1.417
	4	0.829	0.750
1,2-Benzanthracene	9	1.250	2.184
	10	1.186	1.939
	5	1.060	1.510
	8	1.039	1.449
3,4-Benzpyrene**	5*	—	3.000
	6	—	1.667
	7	—	1.667
1,2,5,6-Dibenzanthracene	9*	1.146	1.750
	3	1.040	1.444
	4	1.021	1.361

* Experimentally most reactive position in the molecule.

** S_r of this componud has not yet been obtained.

Table II. The values of $\overline{S}_r+\overline{S}_s$ and para-localization energy in comparison with experimental data of Diels-Alder reaction

Compound	Position	$\overline{S}_r+\overline{S}_s$	Para-localization energy	Experiment
Hexacene	(6, 15)	17.713	3.16	reactive
	(5, 16)	12.857	3.23	
	(1, 4)	4.772	3.61	
Pentacene	(6, 13)	12.500	3.18	reactive
	(5, 14)	10.222	3.23	
	(1, 4)	4.772	3.61	
Naphthacene	(5, 12)	7.600	3.25	reactive
	(1, 4)	4.000	3.62	
1,2-Benznaphthacene	(6, 11)	6.543	3.28	reactive
	(5, 12)	5.889	3.36	
Anthracene	(9, 10)	5.000	3.31	reactive
	(1, 4)	3.250	3.63	
1,2-Benzanthracene	(9, 10)	4.163	3.41	less reactive than anthracene
	(1′, 4′)	2.204	3.78	
1,2,3,4-Dibenzanthracene	(9, 10)	3.539	3.49	less reactive than anthracene
	(5, 8)	2.769	—	
1,2,5,6-Dibenzanthracene	(9, 10)	3.500	3.59	less reactive than anthracene
	(1′, 4′)	2.222	3.79	
Naphthalene	(1, 4)	2.444	3.68	not reactive
Phenanthrene	(1, 4)	2.300	3.77	not reactive
Benzene	(1, 4)	1.504	4.00	not reactive

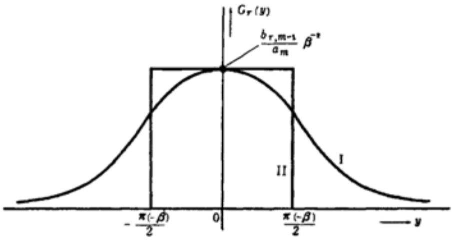


Fig. 1. The curve of the function $G_r(y)$.

integration of curve II by $\bar{S}_r$, it follows that

$$\bar{S}_r=\frac{(-\beta)}{\pi}\int_{-\frac{\pi(-\beta)}{2}}^{\frac{\pi(-\beta)}{2}}G_r(0)\mathrm{d}y$$
$$=\frac{(-\beta)}{\pi}\int_{-\frac{\pi(-\beta)}{2}}^{\frac{\pi(-\beta)}{2}}\frac{b_{r,m-1}}{a_m}\beta^{-2}\,\mathrm{d}y=\frac{b_{r,m-1}}{a_m} \qquad (6)$$

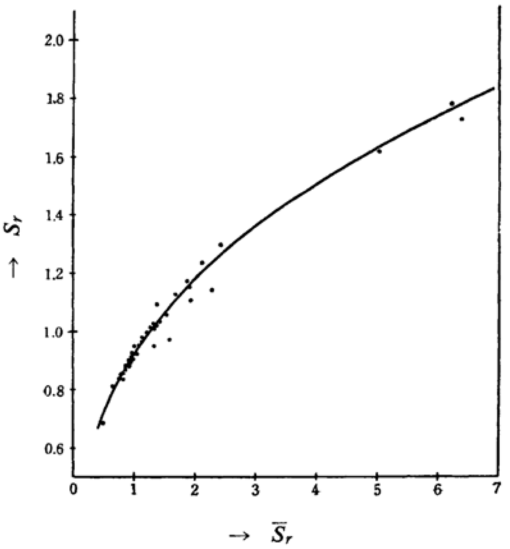
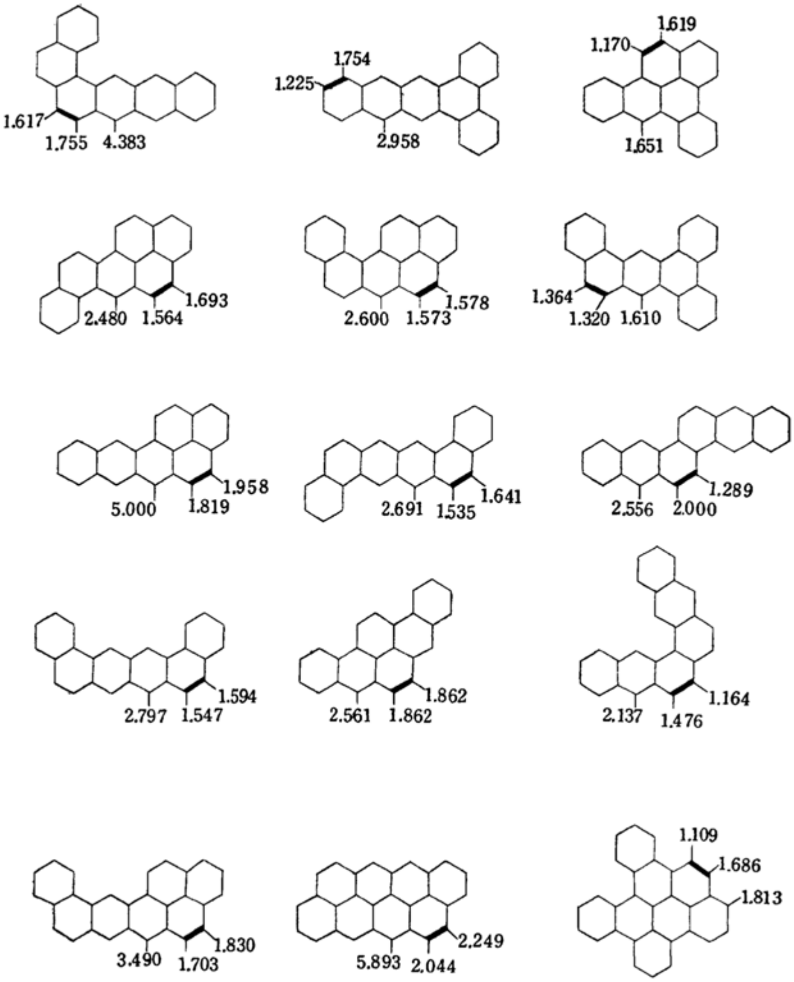


Fig. 2. The relation between S_r and $\bar{S}_r$.



(A thick line in the diagram designates the most reactive bond in the molecule.)

Fig. 3. Prediction of the most reactive position and bond of some condensed aromatic hydrocarbons by the values of $\bar{S}_r$.

Accordingly, it can be calculated very easily even in larger conjugated hydrocarbons. In Appendix I, a simple way of obtaining the values of a_m and $b_{r,m-1}$ is given by using the expansion formulas of secular determinant, wich have already been treated in our previous paper³⁾.

Bearing in mind the result of our previous paper²⁾, we obtain an equation which can relate $\bar{S}_r$ with Dewar's approximate localization energy, l_r. That is,

$$l_r = -\frac{2}{(-\beta)(G_r(0))^{1/2}} = \frac{2}{(\bar{S}_r)^{1/2}} \cdot \beta \qquad (7)$$

Results and Discussion

The calculated values of $\bar{S}_r$ in different positions of some aromatic hydrocarbons are shown in the following tables in comparison with experimental data together with other reactivity indexes.

In Table I, the calculated values of S_r and $\bar{S}_r$ in several hydrocarbons are indicated. The experimentally most reactive positions are shown by an asterisk and the figures corresponding to the predicted most reactive position are shown by heavy asterisks. The larger the value of $\bar{S}_r$ is, the more easily that position is to be attacked. The parallelism between the values of S_r and $\bar{S}_r$ is very intimate, indicating that the latter can be a good approximation to the former. It is seen that $\bar{S}_r$ is also a good index for explaining the relative reactivity between different molecules. For instance, the order of susceptibility of three hydrocarbons to a substituting agent—methylformanilide—is: anthracene > 1, 2-benzanthracene > 1, 2, 5, 6-dibenzanthracene⁴⁾. Furthermore, through the experiment of Fieser and Hershberg⁵⁾ 3, 4-benzpyrene was found to react more readily with lead tetraacetate than 1, 2, 5, 6-dibenzanthracene. This order of reactivity in heterolytic reaction is in agreement with the order in homolytic reaction; that is, Szwarc showed that the order of methyl affinity of some polycondensed aromatic hydrocarbons was: naphthacene > anthracene > 1, 2 - benzanthracene > phenanthrene > naphthalene > benzene⁶⁾. These experimental data are expected from the values of $\bar{S}_r$ in Table I.

Thus, $\bar{S}_r$ itself can be a good reactivity index. But, if one would desire to obtain an approximate value of S_r from the value of $\bar{S}_r$, we can do that by the use of Fig. 2, which

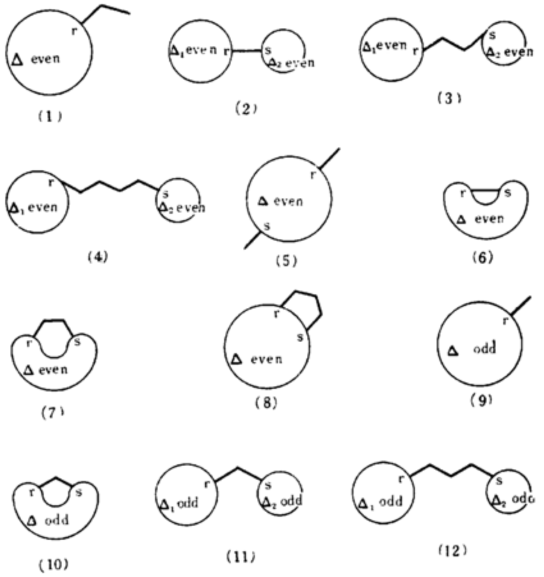


Fig. 4. General formulas for evaluating the value of a_m.

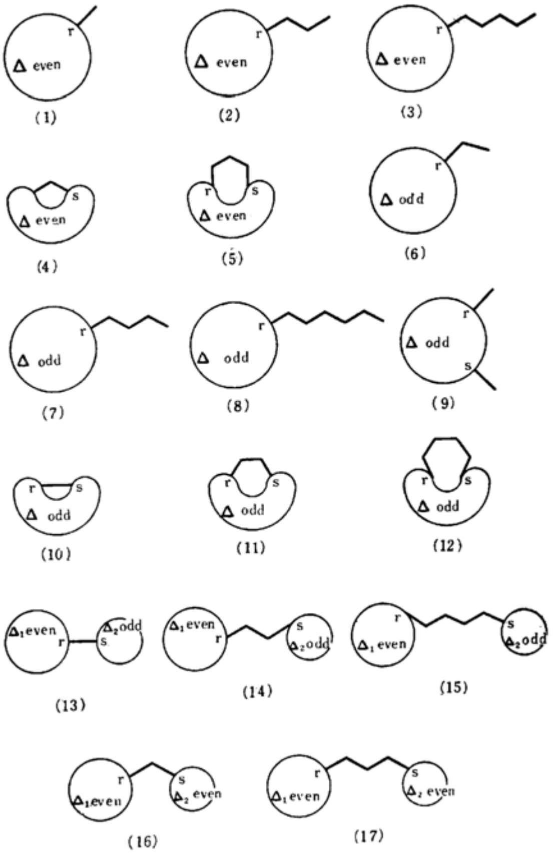


Fig. 5. General formulas for evaluating the value of $b_{r,m-1}$.

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3) K. Fukui, C. Nagata, T. Yonezawa and A. Imamura, This Bulletin, 32, 450 (1959).

4) L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **60**, 2559 (1938).

5) L. F. Fieser and E. B. Hershberg, ibid., 60, 2542 (1938).

6) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

provides the numerical relation between S_r and $\bar{S}_r$.

In Table II, the values of $\bar{S}_r+\bar{S}_s$ are compared with the values of Brown's para localization energy for some polycyclic hydrocarbons. In the simultaneous addition reaction the sum of superdelocalizability at the attacked positions was found to be a good index in our previous study7), accordingly, $\bar{S}_r+\bar{S}_s$ also is expected to be a good index of addition reaction. In Table II a coincidence between the values of $\bar{S}_r+\bar{S}_s$ and para localization energy is observed and both of these indexes explain well the observed data in the Diels-Alder reaction.

In Fig. 3, predictions of the reactivity of some hexa-cyclic and larger condensed hydrocarbons are made. In this figure the molecules treated by Gore8) using Dewar's approximate localization energy method were omitted, and the values of $\bar{S}_r$ at the most reactive position and of the most reactive bond in the molecule are shown. Comparison of these predictions with actual reactivity is hoped to be carried out by future experiments. Calculation of $\bar{S}_r$ of the molecules having as many as eight or more benzene nulei is not tedious. The simple method of calculation proposed in this paper will find its applicability in a discussion of reactivity of larger molecules.

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Appendix I

We derive several formulas which are useful for calculating the values of a_m and $b_{r,m-1}$. By using these formulas, a_m and $b_{r,m-1}$ in larger molecules can be obtained by utilizing those of smaller molecules. Some of these formulas correspond to the expansion formulas of secular determinant previously derived by the present authors3) and the number of each formula corresponds to the number of the type in Figs. 4 and 5.

(A) General formulas for evaluating the value of a_m.

(1) $D(0)=-\Delta(0)$

(2) $D(0)=\Delta_1(0)\Delta_2(0)$

(3) $D(0)=-\Delta_1(0)\Delta_2(0)$

(4) $D(0)=\Delta_1(0)\Delta_2(0)$

(5) $D(0)=\Delta_{rrss}(0)$

(6) $D(0)=\Delta(0)-\Delta_{rrss}(0)-2(-1)^{r+s+1}\Delta_{rs}(0)$

(7) $D(0)=-\Delta(0)+\Delta_{rrss}(0)-2(-1)^{r+s+1}\Delta_{rs}(0)$

(8) $D(0)=\Delta(0)-\Delta_{rrss}(0)-2(-1)^{r+s+1}\Delta_{rs}(0)$
$(\Delta^2_{rs}(0)=-\Delta(0)\Delta_{rrss}(0))$

(9) $D(0)=-\Delta_{rr}(0)$

(10) $D(0)=-\Delta_{rr}(0)-\Delta_{ss}(0)+2(-1)^{r+s+1}\Delta_{rs}(0)$

(11) $D(0)=-\Delta_1(0)\Delta_{2ss}(0)$

(12) $D(0)=\Delta_1(0)\Delta_{2ss}(0)$

The values of a_m in polycondensed aromatic hydrocarbons are easily obtained by classifying these compounds into the following several types.

(B) General formulas for evaluating the value of $b_{r,m-1}$.

(1) $\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\Delta(0)-\left(\frac{\Delta_{rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$

(2) $\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-2\Delta(0)+\left(\frac{\Delta_{rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$

(3) $\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=3\Delta(0)-\left(\frac{\Delta_{rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$

(4) $\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\Delta(0)-\left\{\left(\frac{\Delta_{rr}(\lambda)}{-\lambda}\right)_{\lambda=0}\right.$
$\left.+\left(\frac{\Delta_{ss}(\lambda)}{-\lambda}\right)_{\lambda=0}\right\}+2(-1)^{r+s+1}\left(\frac{\Delta_{rs}(\lambda)}{-\lambda}\right)_{\lambda=0}$

(5) $\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-2\Delta(0)+\left\{\left(\frac{\Delta_{rr}(\lambda)}{-\lambda}\right)_{\lambda=0}\right.$
$\left.+\left(\frac{\Delta_{ss}(\lambda)}{-\lambda}\right)_{\lambda=0}\right\}+\Delta_{rrss}(0)+2(-1)^{r+s+1}\left(\frac{\Delta_{rs}(\lambda)}{-\lambda}\right)_{\lambda=0}$

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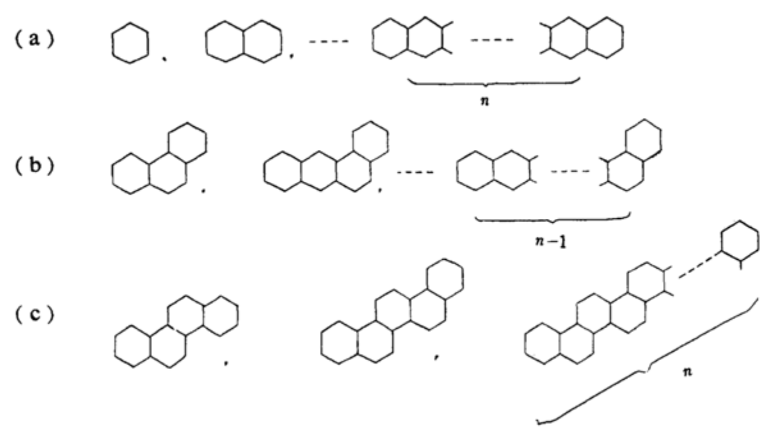
7) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, to be published.

8) P. H. Gore, *J. Chem. Soc.*, **1954**, 3166.

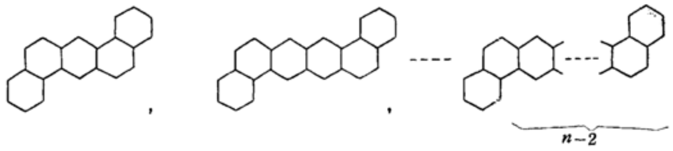


(a) $\Delta(0)=-(n+1)^2$

(b) $\Delta(0)=-(2n-1)^2$

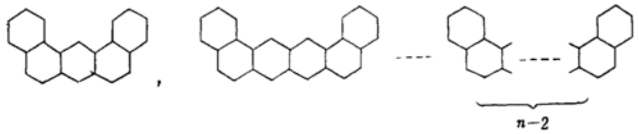
(c) $\Delta(0)=-\frac{1}{5}\left\{\left(\frac{1+\sqrt{5}}{2}\right)^{n+2}-\left(\frac{1-\sqrt{5}}{2}\right)^{n+2}\right\}^2$

(d)



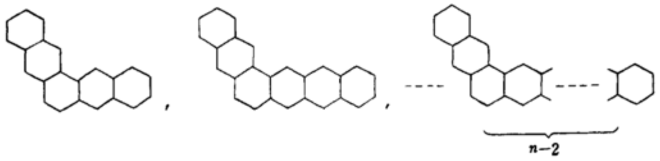
$\Delta(0)=-(4n-8)^2$

(e)



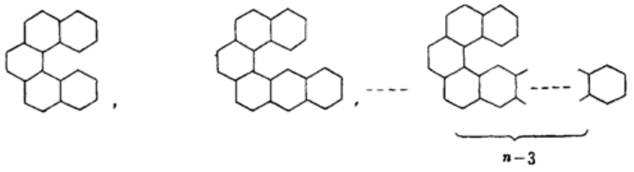
$\Delta(0)=-(4n-8)^2$

(f)



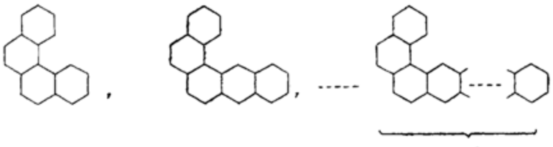
$\Delta(0)=-(3n-5)^2$

(g)



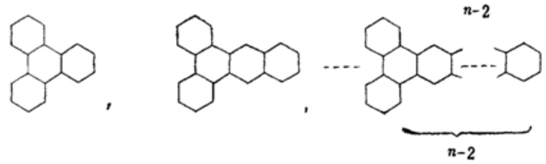
$\Delta(0)=-(5n-12)^2$

(h)



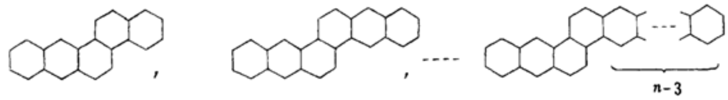
$\Delta(0)=-(3n-4)^2$

(i)



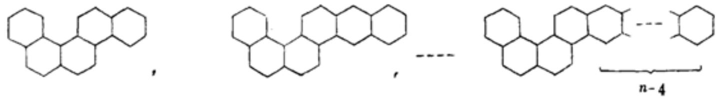
$\Delta(0)=-(4n-7)^2$

(j)



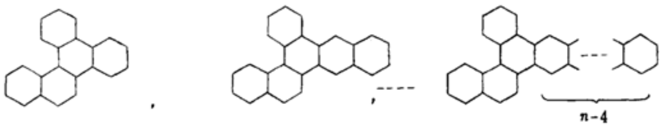
$\Delta(0)=-(4n-9)^2$

(k)



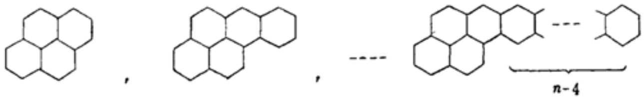
$\Delta(0)=-(5n-12)^2$

(l)



$\Delta(0)=-(6n-16)^2$

(m)



$\Delta(0)=-(3n-6)^2$

(6) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-\Delta_{rr}(0)-\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(7) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=2\Delta_{rr}(0)+\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(8) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-3\Delta_{rr}(0)-\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(9) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-\{\Delta_{rr}(0)+\Delta_{ss}(0)\}+\left(\frac{\Delta_{rrss}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(10) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}-\left(\frac{\Delta_{rrss}(\lambda)}{-\lambda}\right)_{\lambda=0}-2(-1)^{r+s+1}\left(\frac{\Delta_{rs}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(11) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}-\{\Delta_{rr}(0)+\Delta_{ss}(0)\}+\left(\frac{\Delta_{rrss}(\lambda)}{-\lambda}\right)_{\lambda=0}-2(-1)^{r+s+1}\left(\frac{\Delta_{rs}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(12) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\left(\frac{\Delta(\lambda)}{-\lambda}\right)_{\lambda=0}+2\{\Delta_{rr}(0)+\Delta_{ss}(0)\}-\left(\frac{\Delta_{rrss}(\lambda)}{-\lambda}\right)_{\lambda=0}-2(-1)^{r+s+1}\left(\frac{\Delta_{rs}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(13) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\Delta_1(0)\left(\frac{\Delta_2(\lambda)}{-\lambda}\right)_{\lambda=0}-\Delta_{2ss}(0)\left(\frac{\Delta_{1rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(14) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-\Delta_1(0)\left(\frac{\Delta_2(\lambda)}{-\lambda}\right)_{\lambda=0}-\Delta_1(0)\Delta_{2ss}(0)+\Delta_{2ss}(0)\left(\frac{\Delta_{1rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(15) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\Delta_1(0)\left(\frac{\Delta_2(\lambda)}{-\lambda}\right)_{\lambda=0}+2\Delta_1(0)\Delta_{2ss}(0)-\Delta_{2ss}(0)\left(\frac{\Delta_{1rr}(\lambda)}{-\lambda}\right)_{\lambda=0}$$

(16) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=\Delta_1(0)\Delta_2(0)-\left\{\Delta_2(0)\left(\frac{\Delta_{1rr}(\lambda)}{-\lambda}\right)_{\lambda=0}+\Delta_1(0)\left(\frac{\Delta_{2ss}(\lambda)}{-\lambda}\right)_{\lambda=0}\right\}$$

(17) $$\left(\frac{D(\lambda)}{-\lambda}\right)_{\lambda=0}=-2\Delta_1(0)\Delta_2(0)+\left\{\Delta_2(0)\left(\frac{\Delta_{1rr}(\lambda)}{-\lambda}\right)_{\lambda=0}+\Delta_1(0)\left(\frac{\Delta_{2ss}(\lambda)}{-\lambda}\right)_{\lambda=0}\right\}$$

where $\Delta(\lambda)$ and $D(\lambda)$ is the secular determinants of a molecule before and after the growth and $\Delta_{rs}(\lambda)$ and $\Delta_{rrss}(\lambda)$ are the (rs) and $(rrss)$ minors of $\Delta(\lambda)$, respectively.