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Topological Index as Applied to π-Electronic Systems. IV. On the Topological Factors Causing Non-Uniform π-Electron Charge Distribution in Non-Alternant Hydrocarbons*

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The topological factors which cause non-uniform π-electron charge distribution in non-alternant hydrocarbons (NAH's) are discussed. For estimating and analyzing the net-charge density a novel topological index, topological charge density, Q_r^T, is proposed. It is defined as $Q_r^T=\mathrm{Re}(F_{G,r}(1))$, the real part of $F_{G,r}(y)=\Delta_{r,r}(iy)/\Delta(iy)$, where $\Delta(x)$ is the secular determinant of graph G and $\Delta_{r,r}(x)$ is its adjunct with row r and column r struck out. This quantity Q_r^T, corresponding to the Coulson net charge density $Q_r=1-q_r$, is related with the topological indices $\tilde{Z}_G$ and $\tilde{Y}_G$ which are defined in terms of the coefficients of the characteristic polynomial of graph G. As all the newly proposed indices can be enumerated graphically, one can easily estimate the net-charge densities of NAH's.

Coulson and Rushbrooke[1] have proved that the Hückel MO theory predicts uniform π-electron charge distribution in all the alternant hydrocarbons (AH's). Although the structural requirements for uniform π-charge distribution are presently well understood,[1,2] it is not much known[3–6] on the same problem for non-alternant hydrocarbons (NAH's). A number of empirical rules which relate the π-electron charge distribution of NAH's with their structure are collected in Ref. 3, but with an incomplete mathematical justification.[4,7] In Ref. 5 some general consequences of the Coulson integral formula for charge density are presented.

Until recently it has not been recognized[5–11] that useful topological information can be deduced from the Coulson integral representation[12] of several π-electron characteristics of conjugated systems, although parallelism among the several reactivity indices derived from the Hückel MO theory were already proved.[13,14] According to Ref. 12, the total π-electron energy E_π, the bond order p_{rs} between atoms r and s and the charge density Q_r (not the π-electronic but net-charge density) on atom r can be expressed as:

$$E_\pi = \frac{1}{\pi}\int_{-\infty}^{+\infty} F_G(y)\,\mathrm{d}y, \tag{1}$$

$$p_{rs} = \frac{1}{\pi}\int_{-\infty}^{+\infty} F_{G,rs}(y)\,\mathrm{d}y, \tag{2}$$

$$Q_r = \frac{1}{\pi}\int_{-\infty}^{+\infty} F_{G,r}(y)\,\mathrm{d}y, \tag{3}$$

where

$$F_G^*(y) = N - iy\Delta'(iy)/\Delta(iy) \tag{4a}$$

$$F_{G,rs}(y) = -\Delta_{r,s}(iy)/\Delta(iy) \tag{5}$$

$$F_{G,r}(y) = \Delta_{r,r}(iy)/\Delta(iy). \tag{6}$$

Here $i=\sqrt{-1}$ is the imaginary unit and $\Delta(x)\equiv P_G(x)=\det(xI-A)$ is the characteristic polynomial of the molecular graph G with N vertices.[15] A and I are the adjacency matrix and the unit matrix, $(-1)^{r+s}\Delta_{r,s}$ denotes Δ with row r and column s struck out. Note that $\Delta_{r,r}=P_{G\ominus r}$, where $G\ominus r$ is the graph obtained by deletion of vertex r and all the edges incident to it from graph G. Equation 1 holds also for the integrand[9,10]

$$F_G^{**}(y) = y^{-2}\ln|y^N P_G(1/iy)|. \tag{4b}$$

A proof of this relation will be given in Appendix I.

Let us write $P_G(x)$ in the form

$$P_G(x) = \sum_{k=0}^{N} a_k x^{N-k}. \tag{7}$$

Since the relations between the coefficients a_k and the structure of the molecular graph G are nowadays completely elucidated,[16,17] by means of Eqs. 1—3 one can get insight into the topological factors determining E_π, p_{rs} and Q_r. However, this analysis is not simple[14] because of the complicated form of Eqs. 4—6.

We have shown that E_π of a number of conjugated hydrocarbons can be approximated fairly well by $\log\tilde{Z}_G$,[8]

$$E_\pi \doteqdot c\log\tilde{Z}_G \tag{8}$$

where

$$\tilde{Z}_G = \sum_{k=0}^{m}(-1)^k a_{2k} \tag{9}$$

with $m=[N/2]$. It was also found that the value of F_G^{**} for $y=1$ has an analogous behavior as $\tilde{Z}_G$.[18] In particular, numerical analysis shows that E_π is nearly linearly related to $F_G^{**}(1)$. The similar is valid for the function $F_{G,rs}$. That is, $F_{G,rs}$ (1) is shown to be used as a good index for bond orders.[11] This suggests[6] that $F_{G,r}$ (1) may also possess interesting properties for the study of Q_r. In the present paper we would like to demonstrate that this is indeed the case. In order to analyze this problem two different kinds of the topological indices for a given graph are to be defined.

Topological Indices $\tilde{Z}_G$ and $\tilde{Y}_G$

Let us consider the polynomial $P_G(x)$ for $x=i$. According to Eq. 7,

$$P_G(i) = i^N(\tilde{Z}_G+i\tilde{Y}_G) \tag{10a}$$

and

$$P_G(-i) = (-i)^N(\tilde{Z}_G-i\tilde{Y}_G), \tag{10b}$$

where two topological indices are defined as

$$\tilde{Z}_G = \sum_{k=0}(-1)^k a_{2k}{}^{8)} \tag{11a}$$

$$\tilde{Y}_G = \sum_{k=0}(-1)^{k+1} a_{2k+1}. \tag{11b}$$

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TABLE 1. THE CHARACTERISTIC POLYNOMIAL AND THE TOPOLOGICAL INDICES $\tilde{Z}_G$ AND $\tilde{Y}_G$ FOR TYPICAL NON-ALTERNANT HYDROCARBONS

G[a]	$P_G(x)$	$\tilde{Z}_G$	$\tilde{Y}_G$
I	x^4-4x^2+1	6	
	$-2x$		-2
II	$x^6-6x^4+8x^2-1$	16	
	$-2x$		2
III	$x^8-8x^6+19x^4-13x^2+1$	42	
	$-2x$		-2
IV	$x^6-7x^4+11x^2-4$	23	
	$-2x^3+2x$		-4
V	$x^8-9x^6+24x^4-20x^2$	54	
	$-4x^3+8x$		12
VI	$x^{10}-11x^8+41x^6-61x^4+31x^2-4$	149	
	$-2x^5+6x^3-2x$		10
VII	$x^{12}-13x^{10}+62x^8-134x^6+129x^4-45x^2$	384	
	$-4x^5+16x^3-12x$		-32
VIII	$x^6-7x^4+11x^2+3$	16	
	$-4x^3+12x$		-16
IX	$x^8-9x^6+22x^4-10x^2$	42	
	$-2x^5+10x^3-4x$		-16
X	$x^8-9x^6+24x^4-19x^2+5$	58	
	$-2x^5+8x^3-4x$		-14
XI	$x^{12}-14x^{10}+71x^8-165x^6+180x^4-82x^2+9$	522	
	$-2x^7+12x^5-24x^3+14x$		52
XII	$x^{12}-14x^{10}+71x^8-161x^6+158x^4-54x^2+5$	464	
	$-4x^7+22x^5-32x^3+8x$		66
XIII	$x^{14}-16x^{12}+98x^{10}-291x^8+434x^6-305x^4+86x^2-5$	1236	
	$-2x^9+12x^7-18x^5 \quad +4x$		28

a) See Chart 1.

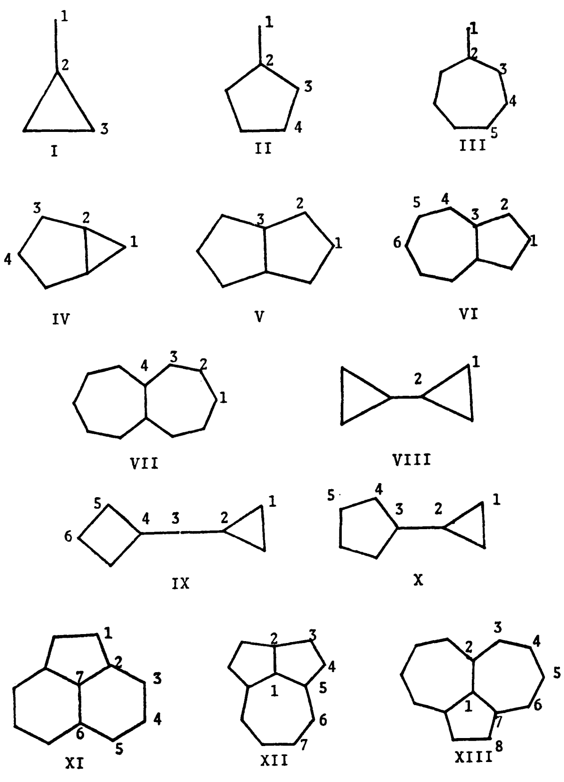


Chart 1

Hence we have

$$F_G^{**}(1) = \ln(\tilde{Z}_G{}^2+\tilde{Y}_G{}^2)^{1/2}. \tag{12}$$

Note that $\tilde{Z}_G$ is always positive,[19] whereas $\tilde{Y}_G$ is zero for an AH and may take a positive or negative value according to the topology of a NAH as shown in Table 1, where the characteristic polynomial and the topological indices $\tilde{Z}_G$ and $\tilde{Y}_G$ for the typical NAH's are given. The following relation can be shown for almost all the NAH's (See the later discussions):

$$\tilde{Z}_G \gg |\tilde{Y}_G|. \tag{13}$$

Thus for an AH we have

$$F_G^{**}(1) = \ln \tilde{Z}_G \qquad (G \in \text{AH}) \tag{14}$$

and for a NAH the relation

$$F_G^{**}(1) \doteq c \ln \tilde{Z}_G \qquad (G \in \text{NAH}) \tag{15}$$

holds as expected.[8,18]

As the Sachs theorem states that[17]

$$a_0 = 1$$
$$a_n = \sum_{S_n}(-1)^{c(s)} \qquad (N \geq n \geq 1), \tag{16}$$

it follows that

$$\tilde{Z}_G = 1 + \sum_{k=1}^{m}(-1)^k \sum_{S_{2k}}(-1)^{c(s)}$$
$$= 1 + \sum_{S_{2k}}(-1)^{n(s)/2+c(s)}. \tag{17}$$

Here $c(s)$ and $n(s)$ denote the number of components and the number of vertices of the directed Sachs graph s. The summation in Eq. 16 runs over the set S_n of all the Sachs graphs with $n(s)=n$ vertices which are contained in the molecular graph G, while in Eq. 17 over the set S_{2k} of all the Sachs graphs with even number of vertices which are contained in *G*. In another terminology[21] a directed Sachs graph is called a linear graph.

If graph *G* has no cycle, namely if *G* is a tree, or an acyclic hydrocarbon, $n(s)=2c(s)$ and Eq. 17 leads to

$$\begin{aligned} \tilde{Z}_G &= 1+\sum_{k=1}\left(\begin{array}{l}\text{number of Sachs graphs}\\ \text{with } k \text{ disjoint edges}\end{array}\right)\\ &= \sum_{k=0}^{m} p(G,k) \qquad (G\in\text{Tree})\\ &= Z_G, \end{aligned} \tag{18}$$

where $p(G, k)$ is the non-adjacent number and Z_G the orignal version of the topological index.[22]

For a non-tree graph Eq. 17 is expressed as

$$\tilde{Z}_G = Z_G + \Delta Z_G \tag{19}$$

$$\Delta Z_G = \sum_{S_{2k}^{\circ}} (-1)^{n(s)/2+c(s)}, \tag{20}$$

where S_{2k}° runs over all the even Sachs graphs containing at least one cycle, and ΔZ_G is called as the aromaticity index.[8] Figures 1 and 2 summarize all the indices, Z_G, ΔZ_G, $\tilde{Z}_G$ and $\tilde{Y}_G$, and illustrates the relation between the Sachs theorem and the topological indices with graph IV as an example. In Ref. 8 it is shown how a combination of two or more cycles contributes to the sign of ΔZ_G. Here analysis will be developed in line with the Sachs formula.

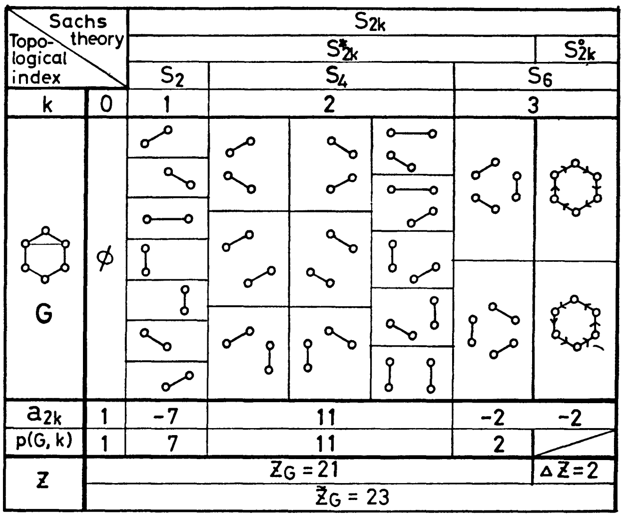


Fig. 1. Relation between the Sachs theorem and the topological indices. Even-Sachs graphs S_{2k} of graph G≡IV are given, which are divided into cycle-including (S_{2k}°) and cycle-excluding (S_{2k}^{*}) graphs. The symmetric part of $P_G(x)=(x^6-7x^4+11x^2-4)+(-2x^3+2x)$ is obtained from this figure. See Table 1 and Fig. 2.

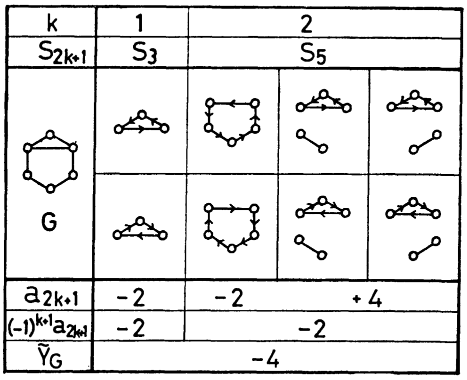


Fig. 2. Relation between $\tilde{Y}_G$ and odd-Sachs graphs, S_{2k+1}, of graph G≡IV. Note that the anti-symmetric part of $P_G(x)=(x^6-7x^4+11x^2-4)+(-2x^3+2x)$ is obtained from this figure. See Fig. 1 and Table 1.

Let s contain $p_0(s)$, $p_1(s)$, $p_2(s)$, and $p_3(s)$ cycles of the size, $4m$, $4m+1$, $4m+2$, and $4m+3$, respectively. Then[10]

$$n \equiv p_1 + 2p_2 + 3p_3 \qquad (\text{mod } 4)$$

$$c \equiv p_0 + p_1 + p_2 + p_3 \qquad (\text{mod } 4)$$

from which one deduces

$$n/2 + c \equiv p_0 + (p_3 - p_1)/2 \quad (\text{mod } 2)$$

or

$$\tilde{Z}_G = \sum_{S_{2k}} (-1)^{p_0+(p_3-p_1)/2} \tag{21}$$

One sees that $\tilde{Z}_G$ is closely related with the cycles contained in the molecular graph. For example, a couple of disjoint $4m$-membered cycles increase the $\tilde{Z}_G$ value as well as a combination of $(4m+1)$- and $(4m+3)$-membered cycles, whereas a couple of $(4m+1)$- or of $(4m+3)$-membered cycles decrease $\tilde{Z}_G$.[8]

If one uses the linear relation (8) the above statement is nothing else but the stability criterion, *i.e.* an extended Hückel rule,[8] for an arbitrary network of conjugated hydrocarbons.

As mentioned earlier, for AH's $a_{2k+1}=0$ for all k and we have $\tilde{Y}_G=0$. If the size of the smallest odd-cycle in G is $2g+1$, one gets $a_1=a_3=\cdots=a_{2g-1}=0$ and $a_{2g+1}=-2n_{2g+1}$, where n_{2g+1} is the number of such cycles.[15,16] Therefore the sign of $\tilde{Y}_G$ is equal to the sign of the term $(-1)^{g+1}a_{2g+1}$. That is,

$$\tilde{Y}_G = \begin{cases} >0 & \text{if the smallest odd cycle in } G \text{ is of the size } 4m+1 \\ <0 & \text{if the smallest odd cycle in } G \text{ is of the size } 4m+3, \end{cases} \tag{22}$$

as shown in Table 1. Hence, $\tilde{Y}_G$ presents a topological index which in a particular way reflects the non-alternant character of a π-electron network. It is important to emphasize that $\tilde{Y}_G$ distinguishes the $(4m+1)$-rings from $(4m+3)$-ones, which seems to be the most important structural factor in determining Q_r.

A consideration analogous to that used for the derivation of Eq. 21 gives

$$\tilde{Y}_G = \sum_{S_{2k+1}} (-1)^{p_0+(p_3-p_1+1)/2} \tag{23}$$

showing that the indices $\tilde{Z}_G$ and $\tilde{Y}_G$ are algebraically closely related. S_{2k+1} is the set of all the directed Sachs graphs with odd number of vertices, which are contained in graph G. However, it is not necessary to draw all these graphs in order to determine the value of $\tilde{Y}_G$. A simple graphical method for the enumeration of $\tilde{Y}_G$ is given in Appendix II.

Topological Charge Density

Following the discussion above it is natural to use the $F_{G,r}$ value for $y=1$ as a kind of topological index for representing the net charge density on atom r in hydrocarbon G.

Substitution of Eq. 10a into Eq. 6 yields

$$F_{G,r}(1) = (\tilde{Z}_{G\ominus r}+i\tilde{Y}_{G\ominus r})/(i\tilde{Z}_G-\tilde{Y}_G), \tag{24}$$

whose real part is expressed as

$$Q_r^{\mathrm{T}} = \mathrm{Re}(F_{G,r}(1)) = \frac{\tilde{Z}_G\tilde{Y}_{G\ominus r}-\tilde{Y}_G\tilde{Z}_{G\ominus r}}{\tilde{Z}_G{}^2+\tilde{Y}_G{}^2} \tag{25}$$

and will be called as the topological (net-) charge density. Although all the quantities in the right-hand side of Eq. 25 are derived from the characteristic polynomial, they can easily be obtained graphically by hand calculation as in Appendix II even without knowing the characteristic polynomial.

TABLE 2. TOPOLOGICAL CHARACTERISTICS OF SUBGRAPHS OF GRAPH IV AND ITS TOPOLOGICAL CHARGE DENSITIES

r	$P_{G\ominus r}(x)$	$\tilde{Z}_{G\ominus r}$	$\tilde{Y}_{G\ominus r}$	Q_r^{T} a)	Q_r b)
1	x^5-5x^3+5x-2	11	2	0.165	0.300
2	x^5-4x^3+3x	8	0	0.059	0.073
3	$x^5-5x^3+4x-2x^2+2$	10	−4	−0.095	−0.215
4	$x^5-5x^3+3x-2x^2$	9	−2	−0.018	−0.072

a) $Q_r^{\mathrm{T}}=\dfrac{\tilde{Z}_G\tilde{Y}_{G\ominus r}-\tilde{Y}_G\tilde{Z}_{G\ominus r}}{\tilde{Z}_G{}^2+\tilde{Y}_G{}^2}$. b) $Q_r=1-q_r$, where q_r is the Coulson charge density calculated from the HMO's.

Examples are shown in Table 2 for graph IV, for which the topological charge density Q_r^{T} is correlated fairly well with the charge density calculated from the Hückel MO's. It is to be noted that the sign of the Q_r value is correctly predicted by Q_r^{T}. Correlation between Q_r and Q_r^{T} was extensively studied for typical NAH molecules. The results are summarized in Table 3, from which the following conclusions are drawn.

TABLE 3. COMPARISON BETWEEN THE TOPOLOGICAL CHARGE DENSITY Q_r^{T} AND THE HÜCKEL CHARGE DENSITY Q_r FOR TYPICAL NON-ALTERNANT HYDROCARBONS

G	r	$\tilde{Z}_{G\ominus r}$	$\tilde{Y}_{G\ominus r}$	a)	Q_r^{T}	Q_r b)
I	1	4	−2	−4	−0.100	−0.488
	2	2	0	4	0.100	0.123
	3	3	0	6	0.150	0.182
II	1	11	2	10	0.038	0.378
	2	5	0	−10	−0.038	−0.047
	3	8	0	−16	−0.062	−0.092
	4	7	0	−14	−0.054	−0.073
III	1	29	−2	−26	−0.015	−0.311
	2	13	0	26	0.015	0.024
	3	21	0	42	0.024	0.058
	4	18	0	36	0.017	0.038
	5	19	0	38	0.021	0.047
IV	1	11	2	90	0.165	0.300
	2	8	0	32	0.059	0.073
	3	10	−4	−52	−0.095	−0.215
	4	9	−2	−10	−0.018	−0.072
V	1	24	2	−180	−0.059	−0.173
	2	27	4	−108	−0.035	0.185
	3	21	0	−252	−0.082	−0.198
VI	1	63	−2	−928	−0.042	−0.047
	2	71	−4	−1306	−0.059	−0.173
	3	55	0	−550	−0.025	−0.027
	4	70	10	790	0.035	0.145
	5	64	6	254	0.011	0.014
	6	67	8	522	0.023	0.130
VII	1	176	−8	2560	0.017	−0.119
	2	168	−6	3072	0.021	0.118
	3	184	−10	2048	0.014	−0.125
	4	144	0	4608	0.031	0.133
VIII	1	10	−4	96	0.188	0.106
	2	8	−4	64	0.125	−0.211
IX	1	21	0	336	0.166	0.295
	2	16	0	256	0.127	0.252
	3	20	−10	−100	−0.050	−0.061
	4	18	−6	36	0.018	0.119
	5	26	−10	−4	−0.002	−0.503
	6	22	−8	16	0.008	0.106
X	1	27	4	610	0.171	0.281
	2	22	4	540	0.152	0.263
	3	20	−10	−300	−0.084	−0.181
	4	26	−10	−216	−0.061	−0.157
	5	24	−10	−244	−0.069	−0.165
XI	1	246	0	−12792	−0.046	−0.066
	2	182	0	−9464	−0.034	−0.044
	3	237	30	3336	0.012	0.091
	4	207	18	−1308	−0.005	−0.008
	5	242	24	−56	−0.000	0.073
	6	167	18	712	0.003	0.002
	7	199	−2	−11392	−0.041	−0.095
XII	1	199	−2	−14062	−0.064	−0.156
	2	173	−8	−15130	−0.069	−0.161
	3	219	20	−5174	−0.024	0.040
	4	220	6	−11736	−0.053	−0.148
	5	171	20	−2006	−0.009	0.060
	6	216	44	6160	0.028	0.114
	7	201	36	3438	0.016	0.093
XIII	1	521	2	−12116	−0.008	0.066
	2	443	50	49396	0.032	0.116
	3	589	22	10700	0.007	−0.048
	4	540	36	29376	0.019	0.101
	5	541	22	12044	0.008	−0.049
	6	587	50	45364	0.030	0.118
	7	448	−20	−37264	−0.024	−0.091
	8	568	−42	−67816	−0.044	−0.122

a) $\tilde{Z}_G\tilde{Y}_{G\ominus r}-\tilde{Y}_G\tilde{Z}_{G\ominus r}$. $\tilde{Z}_G$ and $\tilde{Y}_G$ are given in Tabe 1.
b) $Q_r=1-q_r$.

(1) The topological charge density Q_r^{T} is useful for estimating the relative magnitudes of Q_r in an individual NAH.

(2) The correlation gets worse but still satisfactory for the following three groups of NAH's with i) an NBMO (non-bonding) (V, VII, and IX), ii) an antibonding HOMO (highest occupied) (VIII), and iii) a

bonding LUMO (lowest unoccupied).

(3) For relatively small NAH's (I-IV, VI, X) excluding the above groups, both the relative orders and the signs of Q_r values are correctly predicted by Q_r^{T}.23)

Discussion

As the mathematical form of Q_r^{T} is fairly simple a number of general conclusions are drawn straightforwardly. Equation 25 suggests one to consider Q_r^{T} as a competition between the two terms $\tilde{Z}_G\tilde{Y}_{G\ominus r}$ $(=A_r)$ and $-\tilde{Y}_G\tilde{Z}_{G\ominus r}$ $(=B_r)$. Inspection of Table 3 shows that for almost all the cases, the former term predominates over the latter. Since $\tilde{Z}_G$, as well as $\tilde{Z}_{G\ominus r}$, is always positive and the largest number among the four indices in the expression of Q_r^{T}, the relative magnitude of $\tilde{Y}_{G\ominus r}$ is in parallel with the Q_r^{T} value and hence Q_r. In this sense the first term A_r is local or atomic factor determining the Q_r value. On the other hand, the second term B_r is a global or molecular factor, since its sign is already determined by that of $\tilde{Y}_G$, *i.e.*, by the topology of $\boldsymbol{G}$ (See Eq. 22).

By using this logic one can prove that for a network $\boldsymbol{G}$ in which the only entry of $(4m+3)$-cycle is a triangle, this triangle is positively charged. Choose a vertex r in the triangle. According to Eq. 22 $\tilde{Y}_G$ is negative and B_r positive. If there is no other odd cycle in $\boldsymbol{G}$, $\tilde{Y}_{G\ominus r}$ is zero and so is A_r. Thus Q_r^{T} is positive. If there is at least one $(4m+1)$-cycle, $\tilde{Y}_{G\ominus r}$ is positive and so are A_r and Q_r^{T}. Thus Q_r^{T} is always positive. If a heptagon or a higher-member of $(4m+3)$-cycle coexists with a triangle in network $\boldsymbol{G}$, it can be shown that the electron repulsive power of a triangle is stronger than that of a larger $(4m+3)$-cycle.24) Then unless the conflict between two or more triangles occurs a triangle is shown to be always positive. Although this is a well-known conjecture in the MO theory based on a huge collection of numerical data, there has never been given a general proof for an arbitrary network by conventional perturbation treatment. In order to make the proof complete it will be analyzed in detail in the forthcoming paper that the signs of Q_r^{T} and Q_r are expected to be the same for almost all the cases with a very few exceptions as XIII. Similarly one can conclude that a pentagon is negatively charged in almost all the cases.

In conclusion it will be worth noting that by using the relations (8), (13), and (25), one can get a novel relation

$$Q_r^{\mathrm{T}} \doteq \exp\,(-E_\pi(G)/c)[\tilde{Y}_{G\ominus r}-\tilde{Y}_G\exp\,(-L_r/c)]$$

where $L_r=E_\pi(G)-E_\pi(G\ominus r)$ is the localization energy25,26) of atom r. This interesting relation shows that the value of Q_r is not independent of the stability of the molecule (E_π) and the reactivity of its considered site (L_r).

Appendix I

Proof of Eq. 4b

Given two different functions $F_G^*(y)$ and $F_G^{**}(y)$ for an AH as

$$F_G^*(y) = N - iy\Delta'(iy)/\Delta(iy) \tag{4a}$$

$$F_G^{**}(y) = y^{-2}\ln|y^N P_G(1/iy)|. \tag{4b}$$

and we will show the following equality

$$\int_{-\infty}^{+\infty}F_G^*(y)\mathrm{d}y = \int_{-\infty}^{+\infty}F_G^{**}(y)\mathrm{d}y. \tag{A1}$$

Integration of $F_G^{**}(y)$ by parts one gets

$$\begin{aligned} I &= \int_{-\infty}^{+\infty}F_G^{**}(y)\mathrm{d}y \\ &= [yF_G^{**}(y)]_{-\infty}^{+\infty}-\int_{-\infty}^{+\infty}y\{\mathrm{d}F_G^{**}(y)/\mathrm{d}y\}\mathrm{d}y \\ &= -\int_{-\infty}^{+\infty}y\{\mathrm{d}F_G^{**}(y)/\mathrm{d}y\}\mathrm{d}y \end{aligned} \tag{A2}$$

by noting that $F_G^{**}(y)$ is an even function for AH's.

Differentiation of $F_G^{**}(y)$ with respect to y gives

$$\begin{aligned} \mathrm{d}F_G^{**}(y)/\mathrm{d}y &= -2y^{-3}\ln|y^N P_G(1/iy)| + y^{-3}A(y) \\ &= -2y^{-1}F_G^{**}(y) + y^{-3}A(y), \end{aligned} \tag{A3}$$

where

$$A(y) = N - P_G'(1/iy)/\{iyP_G(1/iy)\}. \tag{A4}$$

Substitution of Eq. A3 into Eq. A2 gives

$$I = 2I - \int_{-\infty}^{+\infty}y^{-2}A(y)\mathrm{d}y. \tag{A5}$$

Thus we have

$$I = \int_{-\infty}^{+\infty}y^{-2}A(y)\mathrm{d}y \tag{A6}$$

Transformation of $y=-Y^{-1}$, $\mathrm{d}y=Y^{-2}\mathrm{d}Y$ gives the relation

$$\begin{aligned} \int_{-\infty}^{+\infty}y^{-2}\mathrm{d}y &= \left[\int_{-\infty}^{0}+\int_{0}^{+\infty}\right]y^{-2}\mathrm{d}y \\ &= \left[\int_{0}^{+\infty}+\int_{-\infty}^{0}\right]\mathrm{d}Y \\ &= \int_{-\infty}^{+\infty}\mathrm{d}Y. \end{aligned} \tag{A7}$$

From Eqs. A4, A6, and A7 one gets

$$I = \int_{-\infty}^{+\infty}F_G^*(y)\mathrm{d}y. \tag{A8}$$

(Q.E.D.)

Appendix II

Graphical enumeration of $\tilde{Y}_G$ value.

The coefficients of the characteristic polynomial $P_G(x)$ are related with the topological index of the parent graph $\boldsymbol{G}$ and its subgraphs $\{G\ominus R_i\}$, where R_i is a cycle or a set of r_i disjoint cycles with a total of n_i vertices, as11,16)

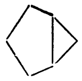
$$\begin{aligned} P_G(x) &= \sum_{k=0}^{m}(-1)^k p(G,k)x^{N-2k} \\ &\quad + \sum_{i}^{R_i\subset G}\sum_{k=0}^{m_i}(-1)^k(-2)^{r_i}p(G\ominus R_i,k)x^{N-n_i-2k}. \end{aligned} \tag{A9}$$

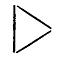
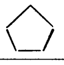
Since the $\tilde{Y}_G$ value is a collection of the coefficients of the terms x^{N-2k-1}, only the contribution by the odd-membered cycles are counted. Then it is straightforward to have

$$\begin{aligned} \tilde{Y}_G &= \sum_{i}^{\substack{n_i=2l_i+1\\ R_i\subset G}}(-1)^{l_i+1}(-2)^{r_i}\sum_{k=0}^{m_i}(-1)^k p(G\ominus R_i,k) \\ &= \sum_{i}^{\substack{n_i=2l_i+1\\ R_i\subset G}}(-1)^{l_i+1}(-2)^{r_i}Z_{G\ominus R_i}, \end{aligned} \tag{A10}$$

which is to be compared with the expression for $\tilde{Z}_G$8)

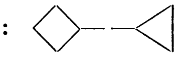
$$\tilde{Z}_G = Z_G + \sum_{i}^{\substack{n_i=2l_i\\ R_i\subset G}}(-1)^{l_i}(-2)^{r_i}Z_{G\ominus R_i}. \tag{A11}$$

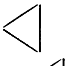
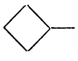
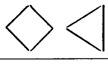
TABLE A1. G 

i	$n_i=2l_i+1$ R_i	l_i	r_i	$G\ominus R_i$	$Z_{G\ominus R_i}$ (A)	$(-2)^{r_i}\times$ $(-1)^{l_i+1}$ (B)	$A\times B$
1		1	1		3	−2	−6
2		2	1	●	1	2	2

$P_G(x)=(x^6-7x^4+11x^2-4)+(-2x^3+2x)$ $\tilde{Y}_G=-4$

$\tilde{Z}_G=1-(-7)+11-(-4)=23$ $\tilde{Y}_G=(-2)-2=-4$

TABLE A2. G: 

i	$n_i=2l_i+1$ R_i	l_i	r_i	$G\ominus R_i$	$Z_{G\ominus R_i}$ (A)	$(-2)^{r_i}\times$ $(-1)^{l_i+1}$ (B)	$A\times B$
1		1	1		10	−2	−20
2		3	2	●	1	4	4

$P_G(x)=(x^8-9x^6+22x^4-10x^2)+(-2x^5+10x^3-4x)$

$\tilde{Y}_G=-16$

$\tilde{Z}_G=1-(-9)+22-(-10)=42$

$\tilde{Y}_G=(-2)-10+(-4)=-16$

In Tables A1 and A2, examples of obtaining $\tilde{Z}_G$ values for graphs IV and IX are given, respectively.

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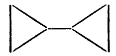
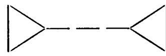
19) This is an outcome of the general relations, $a_0=1$ and $(-1)^k a_{2k}\geq 0$, for which very few exceptions are known such as the case with ,  *etc.*[20]

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