

Regular article

Revisiting superdelocalizability. Mathematical stability of reactivity indices*

Haruo Hosoya, Sayaka Iwata

Department of Information Sciences, Ochanomizu University, Bunkyo-ku, Tokyo 112-8610, Japan

Received: 27 July 1998 / Accepted: 9 September 1998 / Published online: 23 February 1999

Abstract. Superdelocalizability, S_r , defined by Fukui et al. as a variant of reactivity indices in the Hückel molecular orbital scheme for conjugated hydrocarbon molecules is reinvestigated with particular emphasis on its behavior for infinitely large π -electronic systems. Surprisingly, almost all the S_r values of polyacetylene are found to diverge with the size of molecule, while all the S_r values of comb polyene converge to certain values. Similarly, the S_r values of linear polyacene diverge, while those of zigzag polyacene converge. Whether the superdelocalizability for a series of periodic polymers converges or diverges can be predicted, respectively, if the density of states of the infinitely large π -electron network is shown to have non-zero or zero gap at the Fermi level. The behavior of atom-atom polarizability defined by Coulson et al. is also checked and discussed.

Key words: Divergence of superdelocalizability – Large π -electron network – Polyacetylene – Polyacene – Coulson polarizability

1 Introduction

Owing to the rapid and substantial progress in both hardware and software capabilities, it has become possible to trace the detailed paths of elementary reactions by calculating the global and subtle changes of electronic states around the valleys and ridges on a potential surface along some reaction coordinates. Notwithstanding this high-tech development the role of the simple reactivity indices, derived from Hückel molecular orbitals (HMO), has not been totally wiped out from the world of chemical thinking [1, 2]. For example, without the naïve concept of bond order and charge density one cannot interpret or anticipate the stability of molecules and reaction mechanisms in any

branch of chemistry. This information can easily be estimated from the family of polarizabilities defined by Coulson and Longuet-Higgins [3], who have established the mathematical backbone of the HMO method. Fukui and his group pointed out the importance of the HOMO and LUMO under the name of “frontier orbitals” [4] and then proposed a new reactivity index, the superdelocalizability, S_r [5]. Later their theory grew into the theory of HOMO-LUMO interaction [6].

It must be emphasized here that these Hückel-based theories have been applied only to small polycyclic aromatic hydrocarbon molecules no larger than coronene [7]. After extensive studies of these molecules Fukui et al. claimed that the relative magnitudes of the various reactivity indices, π_{rr} (atom-atom polarizability), F_r (free valency), L_r (localization energy), f_r (frontier electron density), and S_r , within a molecule are in parallel with each other [7]. Among these quantities F_r , L_r and f_r have no chance to diverge with an increase in the size of molecules. However, as far as we know, this kind of effect has never been discussed for π_{rr} and S_r .

Recently the usefulness of the Hückel molecular orbital method for calculating and estimating the properties of infinitely large networks such as polyacetylene and graphite was rediscovered [8–10]. In some cases we can manipulate the analytical exposition to allow a plainer discussion. This is a great advantage of the HMO method. Furthermore, by combining a perturbation expansion, a contour integral in the complex plane, and graph theoretical manipulation, Hosoya could derive a mathematical proof of the correctness of the diagrammatic recipe for “organic electron theory” for predicting the direction and extent of π -electron flow in conjugated hydrocarbon networks [11]. In this case the HMO method is used as a proof technique for judging the validity of various hypotheses. In this way we have also been checking the mathematical resilience and range of reliability of the HMO method.

During that study it happened to be found that the superdelocalizability and the atom-atom polarizability for some series of molecules diverge with the size of molecules. Although analysis has not yet been completed, preliminary accounts of the instability of reac-

*Contribution to the Kenichi Fukui Memorial Issue
Correspondence to: H. Hosoya

tivity indices are reported in this paper. In order to establish the reliability of the conventional HMO method and to refine its mathematical structure, and also to explore the limit of its applicability we have to evaluate this instability problem seriously.

2 Superdelocalizability and polarizability

In the HMO scheme the superdelocalizability, S_r , at atom r in a conjugated molecule for an electrophilic reaction is defined by Fukui et al. [5] as

$$S_r = 2 \sum_{n=1}^{\text{occ}} \frac{C_{nr}^2}{x_n} \quad (1)$$

They also defined other types of superdelocalizabilities for nucleophilic and radical reactions by taking different ranges of summation. Among them only the superdelocalizability for electrophilic reactions, Eq. (1), will be considered here, because it can be directly compared with other conventional reactivity indices. Namely, the definition of Eq. (1) is closely related to the bond order, p_{rs}^{HR} , proposed by Ruedenberg and Ham [12] as in the following equation,

$$p_{rs}^{\text{HR}} = 2 \sum_{n=1}^{\text{occ}} \frac{C_{nr} C_{ns}}{x_n} \quad (2)$$

which, however, has been found to be identical with the Pauling's bond order, p_{rs}^{P} , for alternant hydrocarbons without $4n$ -membered rings [12–14]. It is obvious that p_{rs}^{P} cannot take a value larger than unity, and so does p_{rs}^{HR} .

In order to calculate the quantities in Eqs. (1) and (2) for an infinitely large network the following expressions are useful for performing contour integration in the complex plane [3, 7, 14],

$$S_r = -2 \sum_{n=1}^{\text{occ}} \frac{\Delta_{rr}(x_n)}{x_n \Delta'(x_n)} = -\frac{1}{\pi i} \oint_{\gamma} \frac{\Delta_{rr}(z)}{z \Delta(z)} dz \quad (3)$$

and

$$p_{rs}^{\text{HR}} = -2 \sum_{n=1}^{\text{occ}} \frac{\Delta_{rs}(x_n)}{x_n \Delta'(x_n)} = -\frac{1}{\pi i} \oint_{\gamma} \frac{\Delta_{rs}(z)}{z \Delta(z)} dz \quad (4)$$

without recourse to the LCAO MO wavefunctions. Here $\Delta(x)$ is the secular determinant, or its characteristic polynomial, $P_G(x)$,

$$\Delta(x) \equiv P_G(x) \equiv (-1)^N \det(A - xE) \quad (5)$$

which is well reflected from the topological structure of G , a graph corresponding to the carbon atom skeleton of a conjugated hydrocarbon molecule with N carbon atoms [15–18]. Here A is the adjacency matrix of G , and E is the unit matrix of order N . Δ' is the first derivative of Δ with respect to x and Δ_{rs} is the adjunct, or cofactor, of Δ obtained by deleting the elements in r -th row and s -th column and multiplied by $(-1)^{r+s}$.

In this paper, for mathematical simplicity, we will be concerned with only such even bipartite graphs, i.e.,

graphs corresponding to even alternant hydrocarbon molecules that have no $4n$ -membered ring. Then the characteristic polynomial of a bipartite graph G can be expressed as

$$P_G(x) = \sum_{k=0}^m (-1)^k a_k x^{N-2k} \quad (6)$$

with $m = [N/2]$. Note that for almost all practical cases $m = N/2$ and the conjugated hydrocarbon molecule has at least one Kekulé structure. In other words we have $a_m \neq 0$, and thus $P_G(0) \neq 0$.

As the poles of the integrand in Eqs. (3) and (4) are situated along the real axis and also at the origin, the contour γ in the complex plane is chosen as in Fig. 1, where the radii of the inner and outer semicircles are infinitesimally small and infinitely large, respectively. Namely, the contour integration along γ is explicitly expressed as

$$\oint_{\gamma} dz = \lim_{R \rightarrow 0} \left\{ \int_{\theta=-\pi/2}^{\theta=\pi/2} dz + \int_{\theta=\pi/2}^{\theta=-\pi/2} dz + \int_{\theta=-\pi/2}^{\theta=\pi/2} dz + \int_{\theta=\pi/2}^{\theta=-\pi/2} dz \right\} \quad (7)$$

Before explaining the execution of the integration for specific cases let us define the polynomial $q_G(x)$ for graph G associated with its characteristic polynomial as

$$q_G(x) = \sum_{k=0}^m a_k x^{N-2k} \quad (8)$$

From Eqs. (6) and (8) we have

$$P_G(iy) = i^N q_G(y) \quad (9)$$

for a bipartite graph.

The subgraph obtained from G by deleting vertex atom r together with all the edges incident to r has been denoted as $G \ominus r$ [14]. Let us also define another subgraph $G \ominus rs$ by deleting the path from r to s together with all the edges incident to r and s [14]. The following relation can easily be verified:

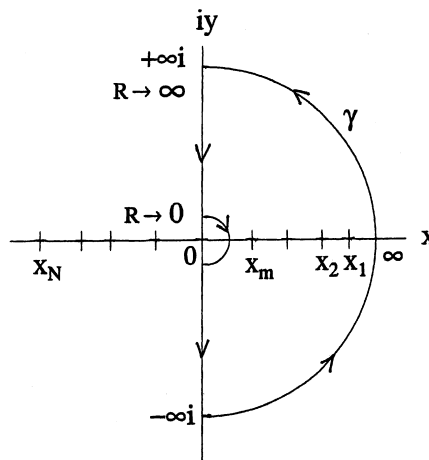


Fig. 1. The contour γ to be integrated in the complex plane for calculating the superdelocalizability

$$S_r = \frac{2}{\pi} \int_0^{\infty} \frac{q_{G\ominus r}(y)}{yq_G(y)} dy . \quad (10)$$

Let us define the integrand of Eq. (10) as $F_{G,r}(y)$.

$$F_{G,r}(y) = \frac{q_{G\ominus r}(y)}{yq_G(y)} = -\frac{P_{G\ominus r}(iy)}{iyP_G(iy)} . \quad (11)$$

Since $G\ominus r$ is associated with a radical, $q_{G\ominus r}(y)$ is a polynomial of odd order and its last term is a_my (a_m is not necessarily non-zero). Then it seems that neither the integrand $F_{G,r}(y)$ nor the integral S_r diverges at least for a graph of finite size.

For later discussion the definition of the atom-atom polarizability and its integral expression are given here [3],

$$\begin{aligned} \pi_{rs} &= 4 \sum_n^{\text{occ}} \sum_m^{\text{vac}} \frac{C_{nr} C_{mr} C_{ns} C_{ms}}{x_n - x_m} \\ &= -\frac{1}{\pi i} \oint_{\gamma} \left\{ \frac{\Delta_{rs}(z)}{\Delta(z)} \right\}^2 dz \\ &= (-1)^{r+s} \frac{2}{\pi} \int_0^{\infty} \left\{ \frac{q_{G\ominus rs}(y)}{q_G(y)} \right\}^2 dy , \end{aligned} \quad (12)$$

where all the quantities are as in Eqs. (1)–(4) and (10). In this case the contour γ is not necessarily a detour around the origin (Eq. (7)) but is simply chosen as

$$\oint_{\gamma} dz = \int_{r=\infty}^{r=-\infty} dz + \int_{\theta=\pi/2}^{\theta=-\pi/2} dz . \quad (14)$$

3 Results

3.1 Linear polyene

Consider a path graph, S_N , or a linear polyene with N carbon atoms. By letting $G = N$ its characteristic polynomial, $P_N(x)$, is expressed as [19]

$$P_N(x) = \sum_{k=0}^m (-1)^k \binom{N-k}{k} x^{N-2k} , \quad (15)$$

with the recursion relation,

$$P_N(x) = xP_{N-1}(x) - P_{N-2}(x) . \quad (16)$$

Then we have

$$q_N(x) = \sum_{k=0}^m \binom{N-k}{k} x^{N-2k} \quad (17)$$

and

$$q_N(x) = xq_{N-1}(x) + q_{N-2}(x) . \quad (18)$$

Let us calculate the superdelocalizabilities, S_r , of a linear polyene **1** at various carbon atoms, where the index r

runs from the terminal atom to the center of the linear chain. The calculated values of S_1 to S_4 and S_c for the smaller linear polyenes are plotted in Fig. 2, where the S_{2l+1} and S_c values increase almost linearly to $\log N$, while S_{2l} values rapidly converge to certain limits. For a given N the magnitude of S_r are ordered as follows:

$$S_1 > S_3 > S_5 > \dots > S_6 > S_4 > S_2 .$$

This oscillating behavior of S_r is gradually damping toward the center of the molecule, but in the central region all the values of S_r seem to gather around S_c .

We can show this divergent character of the S_{2l+1} of linear polyenes in another way. By noticing that $N = 2m$ and using Eq. (17) the value of $F_{N,1}$ at $y = 0$ can be expanded as

$$\begin{aligned} F_{N,1}(0) &= \frac{q_{N-1}(y)}{yq_N(y)} \Big|_{y=0} \\ &= \binom{N-1-(m-1)}{m-1} \Big/ \binom{N-m}{m} \\ &= \frac{m}{N-2m+1} = \frac{N}{2} . \end{aligned} \quad (19)$$

Together with the fact that the first derivative of this F function at $y = 0$ is zero, one can conclude that the S_1 value of polyacetylene diverges. A similar analysis yields that $F_{N,2l+1}(0) = N/2 - l$ and $F_{N,c}(0) \sim N/4$.

The divergent behavior of the S_1 value of polyacetylene can also be verified by the integration of the corresponding F function. Assume that the ratio of the successive q functions converges to $\alpha(x)$ as

$$q_N(x)/q_{N-1}(x) \rightarrow \alpha(x) \quad (20)$$

Then by applying this relation to Eq. (18) we get the following relation for large N ,

$$\alpha(x) = x + 1/\alpha(x) , \quad (21)$$

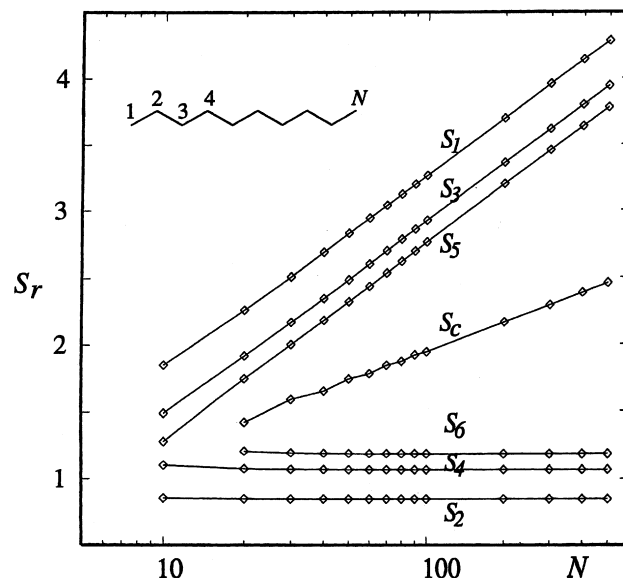


Fig. 2. The S_r values of linear polyacenes

yielding

$$\alpha(x) = \frac{x + \sqrt{x^2 + 4}}{2} \quad (22)$$

By using this, the integral in Eq. (10) for S_1 of polyacetylene can be calculated by

$$S_1 = \frac{2}{\pi} \int_0^\infty \frac{dy}{y\alpha(y)} \quad (23)$$

Numerical integration shows that this is divergent, as is S_c .

On the other hand, the S_2 value of polyacetylene can be calculated as

$$S_2 = \frac{2}{\pi} \int_0^\infty \frac{dy}{\{\alpha(y)\}^2} = \frac{8}{3\pi} = 0.8488 \quad (24)$$

A similar analysis can be performed for π_{rr} of polyacetylene. It is interesting to observe that, when we use Eq. (13), the convergent value of π_{11} of polyacetylene is identical with S_2 of polyacetylene. In our later discussion we will show that the behaviors of these two indices for infinitely large systems vary for certain series of graphs.

3.2 Comb polyene

Experimentally it is rather difficult to isolate and measure the physico-chemical and thermodynamic properties of comb polyenes **2** (Table 1). However, from theoretical studies they are known to be the least stable

Table 1. Convergence of the superdelocalizability (S_r) of comb polyenes, C_{2n+1}

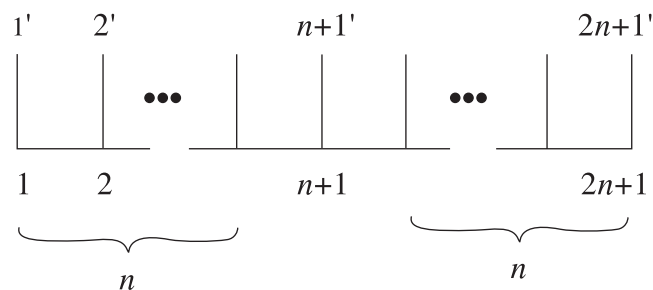
$2n+1^a$	r			
	1^b	1^c	$n+1^b$	$n+1^c$
3	0.9082	1.3165	0.8165	1.6330
5	0.9065	1.3191	0.8373	1.5932
7	0.9065	1.3192	0.8342	1.5980
11	0.9065	1.3192	0.8346	1.5974
$F_{G,r}(y)^d$	$\frac{1}{\beta}$	$\frac{\beta+1}{\beta^2}$	$\frac{\beta}{\beta^2+y^2}$	$\frac{\beta+2}{\beta^2+y^2}$
$\frac{2}{\pi} \int_0^\infty F_{G,r}(y) dy$	0.9065	1.3192	0.8346	1.5974

^a The number of teeth. Total number of carbon atoms is $4n + 2$

^b Position of the root of a tooth

^c Position of the tip of a tooth

^d See Eq. (11). For β see Eq. (29)



isomers among the branched polyenes, and thus have been extensively studied as the counterparts of the most stable linear polyenes [9, 20].

In order to obtain the recursion relation of the characteristic polynomial of the series of comb graphs, C_n , another series of graphs, D_n , as shown in Fig. 3, must be considered. A pair of useful recursion relations connecting these two graphs are given in Fig. 3.

According to the recipe proposed by Hosoya [21] the recursion relation common to C_n and D_n graphs can be straightforwardly obtained as

$$F_n = (x^2 - 1)F_{n-1} - x^2F_{n-2} \quad (F = C, D) \quad (25)$$

We will show that all the superdelocalizabilities of these series of graphs rapidly converge to certain values for infinitely large networks. In Table 1 partial results of S_r values for various atomic positions are given together with the limiting values obtained by the following analysis.

Let us assume that the rational function comprised of the characteristic polynomials of the two successive C_n functions converges to $\beta(x)$ as

$$C_{n+1}/C_n \rightarrow \beta(x) \quad (26)$$

Then according to Eq. (25), $\beta(x)$ is expected to obey

$$\{\beta(x)\}^2 - (x^2 - 1)\beta(x) + x^2 = 0 \quad (27)$$

yielding

$$\beta(x) = \frac{(x^2 - 1) + \sqrt{x^4 - 6x^2 + 1}}{2} \quad (28)$$

which is transformed into

$$\beta(y) = \frac{(y^2 + 1) + \sqrt{y^4 + 6y^2 + 1}}{2} \quad (29)$$

for calculating the integral in Eq. (10).

The form of the analytical formula of the integrand in Eq. (10) depends on the position of the selected carbon atom r . However, by the aid of the above recursion relations between C and D and $\beta(y)$ those integrands can be reduced to the simpler forms given in Table 1. The limiting values were obtained by numerical integration of these integrands. It should be noted that the rate of convergence of the S_r values for comb polyenes is so

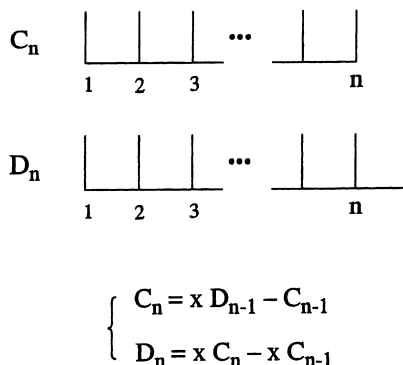
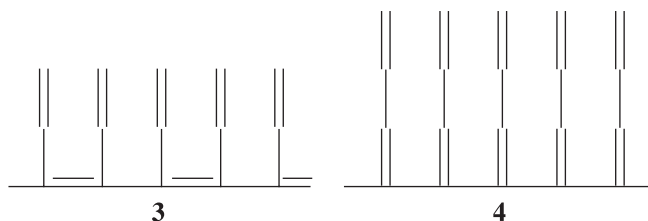


Fig. 3. Comb graph C_n and graph D_n related through recursion relations

rapid that with only ten carbon atoms the limiting values can be obtained to three significant digits, in marked contrast with the $\log N$ divergence of linear polyenes.

We can also show that the polarizabilities of comb polyenes **2** do not converge as those of polyacetylene **1**. Now it becomes clear that both the S_r and π_{rr} of **2**, the comb polyene, do not diverge, while S_{2l+1} diverges and π_{rr} converges in **1**. Between these two isomeric polyenes there are a vast variety of modes of branching in conjugated polyene networks. To clarify this problem, the S_r values of structures **3** and **4** of acyclic polyenes were calculated.



Although the numerical values are not given here, most of the superdelocalizabilities of **3** were found to diverge, while those of **4** converge. We note that the density of states of **1** has no HOMO-LUMO band gap, while a rather big band gap is found between the conduction and valence bands of **2**. By the use of standard techniques [22, 33] we can find the same situation for **3** and **4**. Namely, there is no HOMO-LUMO band gap in the density of states of **3**, while a big band gap is found for **4**.

Thus we can hypothesize that the S_r of a polyene whose density of states has no band gap will diverge with the size of the molecule, while those of a polyene with non-zero band gap will converge to certain finite values. We have already shown that whether a benzenoid polymer has zero or non-zero band gap at the Fermi level in an HMO is determined, respectively, by the existence or non-existence of an NBMO in the hypothetical cyclic monomer or dimer [24]. However, in this case we

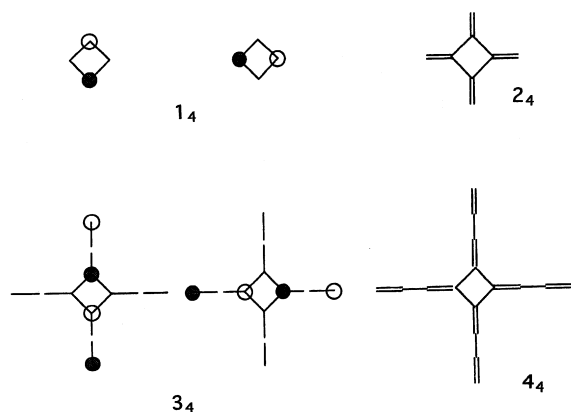


Fig. 4. “Cyclic tetramers”, 1_4 – 4_4 , of polyenes, **1**–**4**. Existence of NBMO’s in 1_4 and 3_4 predicts the zero band gap at the Fermi level of the density of states of **1** and **3**, while the infinitely large **2** and **4** have non-zero band gap as 2_4 and 4_4 have no NBMO. This difference is directly connected to the divergence and convergence of their S_r values

can predict the continuity around the Fermi level from the existence of an NBMO in “cyclic tetramer” as illustrated in Fig. 4. For polarizabilities no such simple rule has ever been discovered.

It is interesting to notice the contrastive behaviors of the S_r of **1** and **2** in parallel with the continuity-discontinuity properties of the phase of the delocalized π -orbitals involved in the cyclic interaction for the electron delocalization from bonds to bonds in **1** and **2** pointed out by Inagaki et al. [25].

3.3 Polyacenes

For our last example we will look at the behavior of the S_r of linear (I_n) and zigzag (W_n) polyacenes, where n refers to the number of hexagonal rings (Fig. 5).

There are two different types of carbon atoms in I_n : those bound to two adjacent carbon atoms (external) and those bound to three adjacent carbons (internal). We can also say that I_n is composed of two connected zigzag hydrocarbon radical chains with $2n + 1$ carbon atoms. It has been known that the value of S_r of a long polyacene increases as one goes from the end of the zigzag edge to the center [5]. Let us denote the superdelocalizability at one of the external carbon atoms in the m -th hexagonal rings as S_{2m} ($m = 1, 2, \dots, (n + 1)/2$). As shown in Fig. 6 the value of S_{2m} for a fixed m slowly increases with n , the length of the polyacene, and their envelope is found to be a straight line, meaning that the superdelocalizability of I_n diverges with the size of molecule. In Table 2 the values of S_{2n+2} of I_{2n+1} polyacenes are given. The S_r values of the external carbon atoms of a hypothetical cyclic polyacene series, \bar{I}_{2n} , were also calculated, and the results are compared in Fig. 6 and Table 2 with those of linear polyacenes. Both the S_r values are found to in-

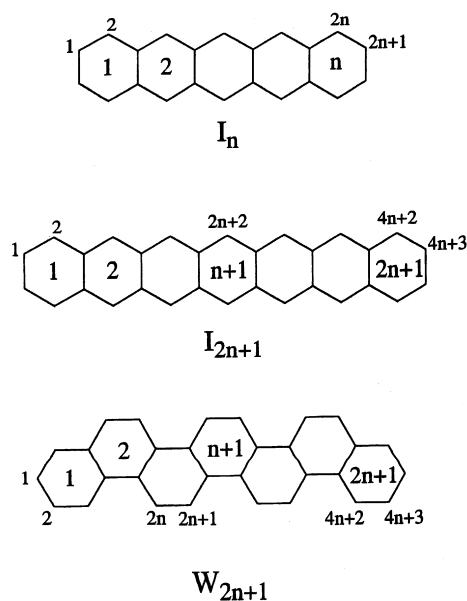


Fig. 5. Linear I_{2n+1} and zigzag W_{2n+1} polyacene graphs, and the numbering of external carbon atoms

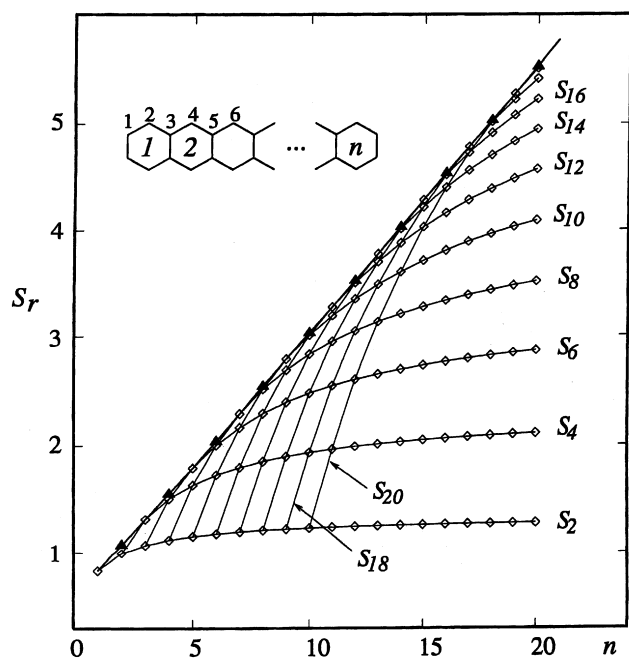


Fig. 6. S_r values of linear (\diamond) and cyclic (\blacktriangle) polyacenes. The S_r values of the latter lie on the straight line envelope of the former

Table 2. Superdelocalizabilities of linear I_{2n+1} and cyclic \bar{I}_{2n} polyacenes

n	S_{2n+2} for I_{2n+1}	S_2 for \bar{I}_{2n}
0	0.8333	—
1	1.3132	1.0763
2	1.7946	1.5523
3	2.2866	2.0397
4	2.7836	2.5347
5	3.2824	3.0329
6	3.7821	3.5322
7	4.2819	4.0320
8	4.7819	4.5319
9	5.2818	5.0318

crease almost linearly with the number of hexagonal rings.

We have also calculated the values of π_{rr} for I_n . The π_{rr} value of the external carbon atom seems to converge to a limiting value, while that of the internal carbon atom seems to diverge with the size of the molecule.

It has been demonstrated previously that I_n and W_n have markedly different band gaps [22, 24]. In fact, I_n has no band gap, while in W_n the band gap is large, even though these two networks are composed of the same butadiene units. Whether the density of states of a given polymer has zero or non-zero band gap has already been studied extensively and can be predicted from the electronic structure of hypothetical cyclic monomer or dimer [23, 24].

The rate of convergence of S_r values in W_n polyacene is so fast that the terminal structure W_{10} is already at the convergent limits of S_r , and the external and internal carbon atoms in the central part of W_n with n above 20 have fixed S_r values as shown in Fig. 7.

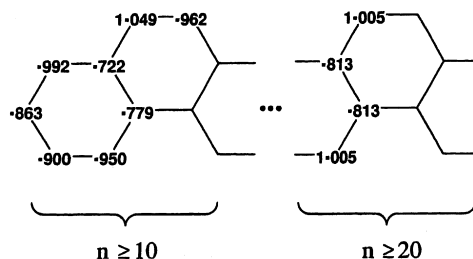


Fig. 7. The limiting values of S_r in the terminal ($n \geq 10$) and central regions ($n \geq 20$) of zigzag polyacene

Although the concept of the superdelocalizability for a conjugated π -electron system was proposed by Fukui et al., in analogy with the Ham-Ruedenberg variant of the bond order, to be used as a reactivity index, its mathematical behavior was found to be closely related to the shape of the density of states near the Fermi level. The Ham-Ruedenberg bond order was found to give exactly the same numerical information as the Pauling bond order derived solely from counting the number of resonance structures [12, 13]. Thus the superdelocalizability should also have some link to the resonance theory. We are currently pursuing this idea.

4 Conclusion

Although the final analysis on the crucial factor of the convergence of polarizabilities has not yet been finished, we can safely conclude that the superdelocalizabilities of infinitely large polymers whose density of π -electron states has no band gap diverges with the size of the polymer. Thus, comparison of the values of superdelocalizability for π -electron conjugated systems should be performed within a molecule or within a group of compounds belonging to the same type of molecules. Hidden mathematical properties of S_r are worthy of further analysis.

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Note added in proof

After submission of this manuscript the author was informed by Prof. Isihara that he has pointed out the divergent property of the superdelocalizability for linear polyene based on the discussion quite different from the present treatment. The author is greatly indebted to him for this important information.

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