Wheland Polynomial. I. Graph-theoretical Analysis of the Contribution of the Excited Resonance Structures to the Ground State of Acyclic Polyenes

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(Received January 30, 1979)

The Wheland polynomials, the set of the numbers, $w(G,j)$, of the j-th excited resonance structures, for a number of acyclic polyenes were calculated. The relations of $w(G,j)$ with the non-adjacent numbers, $p(G,k)$, topological index, Z_G, and the total π-electronic energy, E_π, were analyzed in detail for linear polyenes. For branched polyenes similar results were obtained, and it was found and proved that E_π is linearly related with the number of Dewar (singly excited)structures. Method for the numbering of atoms to generate the canonical resonance structures was discussed.

Recently a number of interesting relations between the Hückel molecular orbital (MO) and resonance or valence bond (VB) theories have been found and/or reinterpreted by the application of the graph theory (GT) and combinatorial theory to the electronic structures of conjugated molecules.[1-7] The essence of these lines of studies does not lie in the accurate prediction of certain properties of molecules by the use of many sophisticated parameters and approximations but in the physical interpretation of the empirical relations and also in the analysis of the mathematical structures of the theories which have been proposed.

Enumeration of the resonance structures of conjugated hydrocarbons is one of the revived problems, yielding abundant crops.[1,3,8-13] Although it has long been pointed out that as the size of the conjugated molecule increases the weight of the contribution of the Kekulé structures in the ground state rapidly decreases, the total π-electronic energy E_π of conjugated hydrocarbons is shown to be closely related to the number of the Kekulé structures, K.[2,3,7] From quite a different point of view one of the present authors has proposed the non-adjacent numbers $p(G,k)$ and topological index for characterizing the topological structure of a graph,[14] and found the relations of the $p(G,k)$ numbers with K and D, the number of the (singly excited) Dewar structures.[5] Further, the topological index Z_G, namely, the sum of the $p(G,k)$ numbers, for a tree graph is known to be closely related to the E_π value of the corresponding hydrocarbon molecule.[15] Then there must be also some useful relations between E_π and the numbers of higher excited resonance structures.

However, very few studies have been done on the analysis of the excited resonance structures. An effective method (hereinafter called as Wheland polynomial) for enumerating the set of numbers of the canonical resonance structures was proposed by Wheland[8] in 1935 but has been overlooked ever since.[16] The aims of the present paper are to generate the Wheland polynomials for a number of tree graphs, *i.e.*, the carbon atom skeletons of acyclic conjugated hydrocarbons, to find out the relations among these quantities of different origins, *i.e.*, of VB, MO, and GT, and to analyze these relations.

Definitions and Calculations[8]

Consider $N(=2n)$ circularly arranged and numbered points representing the carbon-atom skeleton of either an annulene or a linear polyene, and draw n non-crossing bonds. We get $C_n=(2n)!/\{n!(n+1)!\}$[17] patterns as exemplified in Fig. 1a for the case with $N=6$. When each pattern is projected back onto the σ-bond skeleton of the structural formula of the conjugated molecule concerned, a resonance structure is obtained. The degree of excitation of each resonance structure is defined as the number of "ineffective" or long bonds. The $(2n)!/\{n!(n+1)!\}$ resonance structures thus obtained form a set of the canonical structures.

The Wheland polynomial $W_G(x)$ is defined as

$$W_G(x) = \sum_{k=0}^{m} w(G, k)x^k \qquad (1)$$

where $w(G,k)$ is the number of the k-th excited structures for a given set of the canonical structures of graph G. Given any graph with N numbered points, a set of the canonical structures are automatically obtained by the above procedure (see Fig. 1b). All the $w(G,k)$ numbers in this paper were obtained by computers.[18] Note that the set of $w(G,k)$ numbers, or the Wheland polynomial $W_G(x)$ depends on the numbering of points, or atoms, as shown in Fig. 1c. Among a set of various $W_G(x)$ expressions for a given graph, let the highest priority be given to the one which would be the first entry when aligned in the "dictionary order." Such $W_G(x)$ may have the property that, if a proper value δ is chosen such that $0<\delta\ll 1$, the value of $W_G(\delta)$ is the largest among the set of the possible numberings. In Appendix some discussion on the numbering will be given.

Results and Discussion

In order to clarify the relation between the Wheland polynomial and the π-electronic energy of conjugated hydrocarbons, first the results of the linear polyenes will be analyzed in detail, and the effect of the branching will be discussed later.

Linear Polyene. Let us denote a linear polyene with n double bonds, or $2n(=N)$ sp^2 carbon atoms, by $\bar{n}$.[19] The Wheland polynomials for smaller members

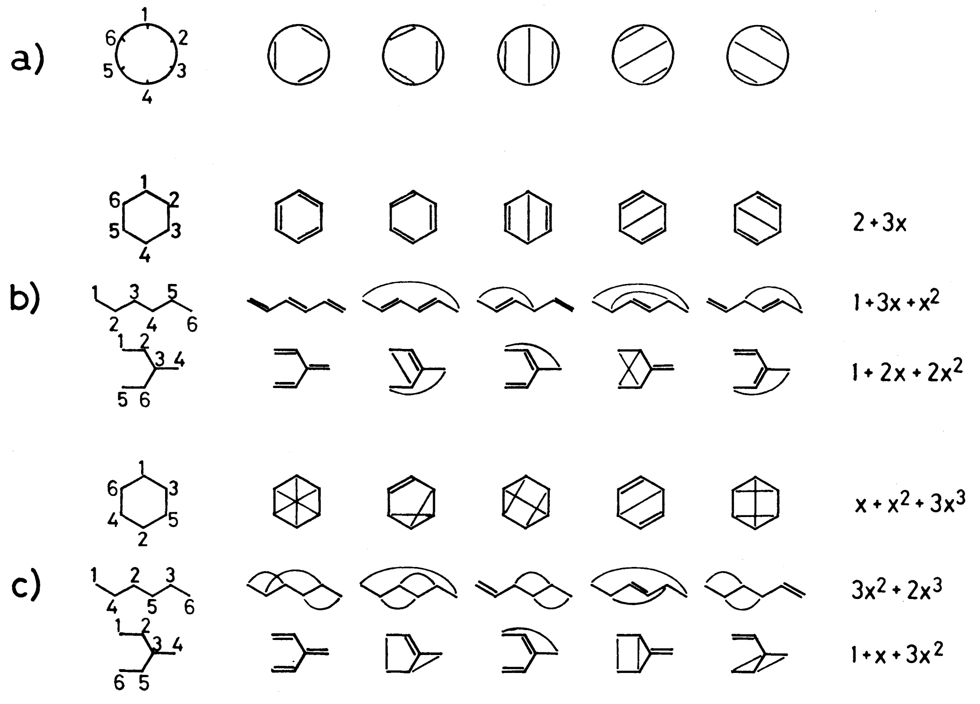


Fig. 1. Generation of the canonical set of the resonance structures and Wheland polynomial.
a) The standard patterns.
b) The Wheland polynomials of the highest priority obtained by the proper numbering.
c) The Wheland polynomials obtained by the improper numbering.

TABLE 1. COEFFICIENTS OF THE WHELAND POLYNOMIAL FOR LINEAR POLYENES[a)]

n[b)]	$w(\bar{n}, j)$									$\sum w(\bar{n}, j)$[c)]
	$j=0$	1	2	3	4	5	6	7	8	
0	1									1
1	1									1
2	1	1								2
3	1	3	1							5
4	1	6	6	1						14
5	1	10	20	10	1					42
6	1	15	50	50	15	1				132
7	1	21	105	175	105	21	1			429
8	1	28	196	490	490	196	28	1		1430
9	1	36	336	1176	1764	1176	336	36	1	4862

a) $W_G(x)=\sum_{j=0} w(G, j)x^j$. b) Number of double bonds. c) Catalan number.

TABLE 2. NON-ADJACENT NUMBERS AND TOPOLOGICAL INDEX FOR LINEAR POLYENES[a)]

n[b)]	$p(\bar{n}, k)$										$Z_{\bar{n}}=p(\bar{n}, k)$[c)]
	$k=0$	1	2	3	4	5	6	7	8	9	
0	1										1
1	1	1									2
2	1	3	1								5
3	1	5	6	1							13
4	1	7	15	10	1						34
5	1	9	28	35	15	1					89
6	1	11	45	84	70	21	1				233
7	1	13	66	165	210	126	28	1			610
8	1	15	91	286	495	462	210	36	1		1597
9	1	17	120	455	1001	1287	924	330	45	1	4181

a) $P_G(x)=\sum_{k=0} p(G, k)\, x^k$. b) Number of double bonds. c) $Z_{\bar{n}}$ is the $2n$-th Fibonacci number, F_{2n}. $F_n=F_{n-1}+F_{n-2}$ with $F_0=F_1=1$.

of the series are given in Table 1, from which the general expressions are derived,

$$W_{\bar{n}}(x) = \sum_{j=0}^{n-1} w(\bar{n},j)x^j \qquad (n>0) \tag{1'}$$

$$w(\bar{n},j) = \frac{n!(n-1)!}{j!(j+1)!(n-j)!(n-j-1)!} \tag{2}$$

$$= \frac{1}{n}\binom{n}{j}\binom{n}{j+1}.$$

By definition $W_{\bar{0}}(x)=1$.

The following relations have been known.[8)]

$$W_{\bar{n}}(x) = W_{\overline{n-1}}(x) + x\sum_{j=1}^{n-1} W_{\bar{j}}(x)W_{\overline{n-j-1}}(x), \tag{3}$$

$$W_{\bar{n}}(1) = \sum_{j=0}^{n-1} w(\bar{n},j) = \frac{(2n)!}{n!\,(n+1)!}, \tag{4}$$

or

$$\frac{1}{n}\sum_{j=0}^{n-1}\binom{n}{j}\binom{n}{j+1} = \frac{(2n)!}{n!\,(n+1)!}. \tag{4'}$$

The non-adjacent number $p(\mathrm{G},k)$, *i.e.*, the number of ways for choosing k disjoint lines, for linear polyene $\bar{n}$ is given by[14)]

$$p(\bar{n},k) = \binom{2n-k}{k}, \tag{5}$$

or

$$p(\bar{n},n-k) = \binom{n+k}{n-k}. \tag{6}$$

The topological index Z_{G} is defined as the sum of the $p(\mathrm{G},k)$'s for graph G,[14)]

$$Z_{\mathrm{G}} = \sum_{k=0}^{m} p(\mathrm{G},k). \tag{7}$$

For a linear polyene

$$Z_{\bar{n}} = \sum_{k=0}^{n} p(\bar{n},k) = \sum_{k=0}^{n} p(\bar{n},n-k). \tag{8}$$

These values are given in Table 2.

In order to get the relation between $w(\mathrm{G},k)$ and $p(\mathrm{G},k)$, try to take the summation of $w(\mathrm{G},k)$ with weight as

$$S = \frac{k!(k+1)!}{(2k)!}\sum_{j=0}^{k}\binom{n-j}{k-j}w(\bar{n},j)$$

$$= \frac{(k+1)!(n-1)!}{(2k)!(n-k)!}\sum_{j=0}^{k}\binom{n}{j+1}\binom{k}{k-j}. \tag{9}$$

By using the Vandermonde convolution formula[20)]

$$\binom{n+p}{m} = \sum_{k=0}^{m}\binom{n}{m-k}\binom{p}{k}, \tag{10}$$

one gets

$$\sum_{j=0}^{k}\binom{n}{j+1}\binom{k}{k-j} = \binom{n+k}{k+1}, \tag{11}$$

which gives

$$S = \binom{n+k}{n-k}.$$

That is, Eqs. 6 and 9 are found to be equal,

$$p(\bar{n},n-k) = \frac{k!(k+1)!}{(2k)!}\sum_{j=0}^{k}\binom{n-j}{k-j}w(\bar{n},j). \tag{12}$$

This is the relation between the coefficients of the Wheland polynomial and the non-adjacent numbers for a linear polyene. Similarly we get

$$w(\bar{n},j) = \sum_{k=0}^{k}(-1)^{j-k}\frac{(2k)!}{k!(k+1)!}\binom{n-k}{j-k}p(\bar{n},n-k). \tag{13}$$

Specifically, the following relations for a linear polyene are to be noted:

$$w(\bar{n},0) = K \quad \text{(number of "Kekulé structures")}$$

$$= p(\bar{n},n) \tag{14}$$

$$w(\bar{n},1) = D \quad \text{(number of "Dewar structures")}$$

$$= p(\bar{n},n-1) - n\,p(\bar{n},n) \tag{15}$$

$$w(\bar{n},2) = D_2 \quad \text{(number of "double Dewar structures")}$$

$$= 2p(\bar{n},n-2) - (n-1)p(\bar{n},n-1)$$

$$+ \frac{n(n-1)}{2}p(\bar{n},n). \tag{16}$$

By substituting Eq. 12 into Eq. 8, followed by the substitution $k=j+i$, one gets the relation between the topological index and the coefficients of the Wheland polynomial for a linear polyene as

$$Z_{\bar{n}} = \sum_{k=0}^{n}\sum_{j=0}^{k}\frac{k!(k+1)!}{(2k)!}\binom{n-j}{k-j}w(\bar{n},j)$$

$$= \sum_{j=0}^{n} C(n,j)\,w(\bar{n},j) \tag{17}$$

$$C(n,j) = \sum_{i=0}^{n-j}\frac{(j+i)!(j+i+1)!}{(2j+2i)!}\binom{n-j}{i}. \tag{18}$$

For an acyclic hydrocarbon, whose carbon atom skeleton is expressed as a tree graph, the total π-electronic energy E_π calculated by the Hückel molecular orbital method is known to be related to Z_{G} as[15)]

$$E_\pi = A\ln Z_{\mathrm{G}} \qquad (\mathrm{G}\in\text{tree}), \tag{19}$$

which, by the substitution of Eq. 17, yields

TABLE 3. WEIGHT OF THE COEFFICIENTS OF THE WHELAND POLYNOMIAL IN THE π-ELECTRONIC ENERGY FOR LINEAR POLYENES

n	$C(n,j)$								
	$j=0$	1	2	3	4	5	6	7	8
0	1.0000								
1	2.0000	1.0000							
2	3.5000	1.5000	0.5000						
3	5.7000	2.2000	0.7000	0.2000					
4	8.8714	3.1714	0.9714	0.2714	0.0714				
5	13.3810	4.5095	1.3381	0.3667	0.0952	0.0238			
6	19.7219	6.3409	1.8314	0.4933	0.1266	0.0314	0.0076		
7	28.5554	8.8335	2.4926	0.6612	0.1679	0.0413	0.0099	0.0023	
8	40.7648	12.2094	3.3759	0.8833	0.2221	0.0542	0.0129	0.0030	0.0007

$$E_\pi = A \ln \sum_{j=0}^{n} C(n,j)w(\bar{n},j). \tag{20}$$

From this equation one can obtain the contribution or weight of each coefficient $w(\bar{n},j)$ of the Wheland polynomial to the total π-electronic energy.

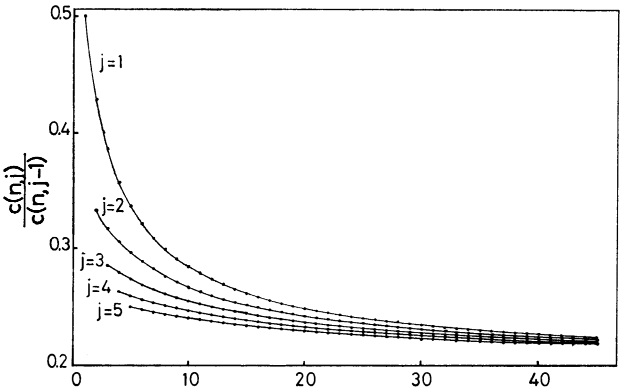


Fig. 2. Convergence of the ratio $C(n, j)/C(n, j-1)$ for larger polyenes. See also Table 3.

The values of $C(n,j)$ for smaller n and j's are given in Table 3, which shows a rapid decrease of $C(n,j)$ with the increase of j. Further, as seen in Fig. 2 the ratio of $C(n,j)$ to $C(n,j-1)$ converges to a certain value for larger n, or

$$C(n,j) \rightarrow C(n,0)\alpha^j, \tag{21}$$

with the value of α a little above 0.2.

By the substitution of Eq. 21 into Eq. 20, it turns out that E_π can approximately be expressed in terms of the Wheland polynomial,

$$E_\pi = A \ln \{C(n,0)W_{\bar{n}}(\alpha)\}, \tag{22}$$

or simply as

$$E_\pi = a \ln W_G(\alpha) + b \quad (\alpha=0.2). \tag{23}$$

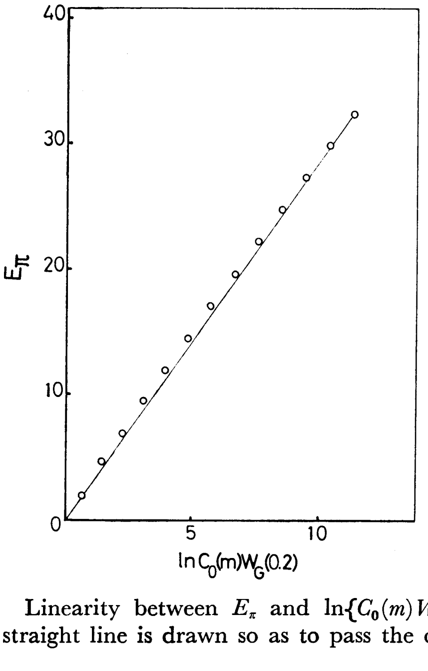


Fig. 3. Linearity between E_π and $\ln\{C_0(m)W_G(0.2)\}$. The straight line is drawn so as to pass the origin.

Although Eq. 22 has been derived for larger n, numerical calculation shows that this relation is also fairly valid even for smaller linear polyenes (Fig. 3). Later it will be shown that Eq. 23 can also be applied to branched polyenes.

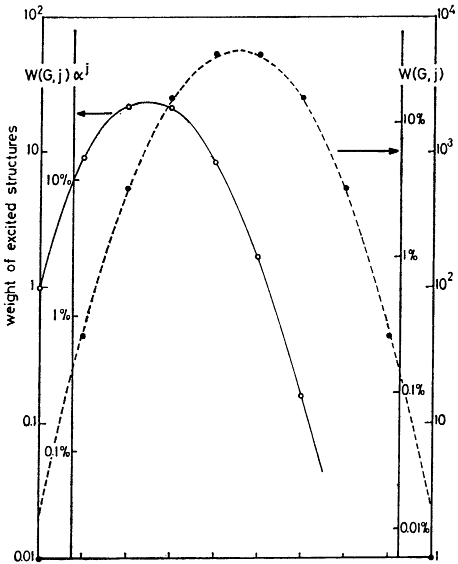


Fig. 4. Dependence of $w(G, j)$ and $w(G, j)\alpha^j$ on the degree of excitation for polyene $C_{20}H_{22}$.
—•—: $w(G,j)$.
------: Gaussian curve, $5600\exp\{-0.392(j-4.5)^2\}$, to fit the $w(G,j)$ values.
—o—: $w(G,j)\alpha^j$.

Among the whole spectrum of the resonance structures scanned with the order of excitation, one can analyze what is the largest contribution to the energy of the ground state. The values of $w(G,j)$ and $w(G,j)\alpha^j$ with $\alpha=0.2$ for linear polyne $\overline{10}$ are plotted in Fig. 4, where two remarkable features are seen. Although a rigorous proof can not be obtained yet, the smoothed curve of $w(\bar{n},j)\alpha^j$ against j is symmetric with respect to $j=n/2$ and very close to that of the Gaussian curve, $\exp(-x^2)$ (see the broken line). Next the peak of the smoothed curve of $w(\bar{n},j)\alpha^j$ is found at about $j=0.3n$. This can be proved as follows.

For larger n the value of j at which the curve $w(\bar{n},j)\alpha^j$ is an extremum is the root of the following equation

$$\frac{1}{n}\binom{n}{j}\binom{n}{j+1}\alpha^j = \frac{1}{n}\binom{n}{j-1}\binom{n}{j}\alpha^{j-1},$$

and is found to be approximately as

$$j = \sqrt{\alpha}\,n/(\sqrt{\alpha}+1),$$

or

$$j/n = \sqrt{\alpha}/(\sqrt{\alpha}+1) = 0.309, \tag{24}$$

if α takes 0.2.

As has been pointed out earlier,[21] this result confirms that the contributions of the Kekulé structures and even of the lower excited structures get vanishingly small with the increase of the size of the molecule. However, it might still be possible that the numbers of the lower

TABLE 4. TOPOLOGICAL CHARACTERISTICS OF HEXATRIENE AND OCTATETRAENE ISOMERS

Isomer[a)]	b)	$w(G,j)$					$p(G,k)$					Z_G	E_π[c)]
		$j=0$	1	2	3	4	$k=0$	1	2	3	4		
3-1	I_3	1	3	1			1	5	6	1		13	6.9879
3-2	A_3	1	2	2			1	5	5	1		12	6.8990
4-1	I_4	1	6	6	1		1	7	15	10	1	34	9.5175
4-2	B_4, C_4	1	5	5	3		1	7	14	9	1	32	9.4459
4-3	A_4	1	4	8	0	1	1	7	14	8	1	31	9.4093
4-4	D_4	1	3	9	1		1	7	13	7	1	29	9.3317

a) See Chart 1 for the structure and numbering of carbon atoms. b) X_m refers to the polyene of the series X with m double bonds. See Chart 3. c) Total Hückel π-electronic energy in β units.

TABLE 5. TOPOLOGICAL CHARACTERISTSCS OF DECAPENTAENE ISOMERS

Isomer[a)]	b)	$w(G,j)$					$p(G,k)$						Z_G	E_π[c)]
		$j=0$	1	2	3	4	$k=0$	1	2	3	4	5		
5-1	I_5	1	10	20	10	1	1	9	28	35	15	1	89	12.0534
5-2	B_5	1	9	15	14	3	1	9	27	32	14	1	84	11.9852
5-3	C_5	1	8	18	11	4	1	9	27	32	13	1	83	11.9669
5-4	A_5	1	7	21	8	5	1	9	27	31	12	1	81	11.9375
5-5	—	1	8	14	18	1	1	9	26	30	13	1	80	11.9248
5-6	—	1	6	22	8	5	1	9	27	31	11	1	80	11.9180
5-7	E_5,F_5	1	6	20	12	3	1	9	26	29	11	1	77	11.8747
5-8	—	1	6	17	11	6	1	9	26	28	11	1	76	11.8636
5-9	D_5	1	5	22	12	2	1	9	26	28	10	1	75	11.8428
5-10	—	1	5	20	8	7	1	9	26	27	10	1	74	11.8314
5-11	—	1	4	19	13	4	1	9	25	25	9	1	70	11.7636

a) See Chart 2 for the structure and numbering of carbon atoms. b) X_m refers to the polyene of the series X with m double bonds. See Chart 3. c) Total Hückel π-electronic energy in β units.

excited structures are good indicators for E_π. This will be the case if the shape of the curve $w(G,j)\alpha^j$ does not appreciably change from isomer to isomer or does change somewhat systematically so that some cancellation occurs.

Branched Polyenes. Analysis on the relation between the Wheland polynomial and the electronic energy can be extended to branched polyenes in two different aspects, *i.e.*, difference among isomers and general properties within a series of branched hydrocarbons. Questions are: 1) does relation 23 hold for a group of isomers, and 2) does Eq. 12 or 13 hold for a series of branched polyenes?

The Wheland polynomials for smaller branched polyenes are given in Tables 4 and 5, where the $p(G,k)$ numbers, topological index, and the total π-electronic Hückel energy E_π are also given. Here the isomers are numbered according to the values of E_π. It is to be noted that with only one exception (between compounds 5-4 and 5-5) for each group of isomers with $n \leq 5$ this is just the order of decreasing the number of the first excited or Dewar structures, $w(G,1)=D$. For the group of isomers with the same D, the larger the number of the second excited or double Dewar structures, $w(G,2)=D_2$, the larger the E_π value.

To be more quantitative, the E_π values of the decapentaene isomers are plotted against the $\ln\{W_G(0.2)\}$ values in Fig. 5a (see also Table 5). The linearity is a little worse than the remarkably good plot of $E_\pi-\ln Z_G$ (Fig. 5c), but unexpectedly good in spite of the several assumptions and approximations we have made. Similar linearity, though a little more scattered than the smaller polyenes, was obtained for the twenty four isomers of dodecahexaenes. It was found, further, that the contributions of only the first and second excited structures, $\alpha D+\alpha^2 D_2$, can predict the order of E_π value as well as the $\ln\{W_G(\alpha)\}$ value with $\alpha=0.2$ (see Fig. 5b). Namely, for a group of isomers of acyclic polyenes, the E_π values are linearly related with the numbers of the

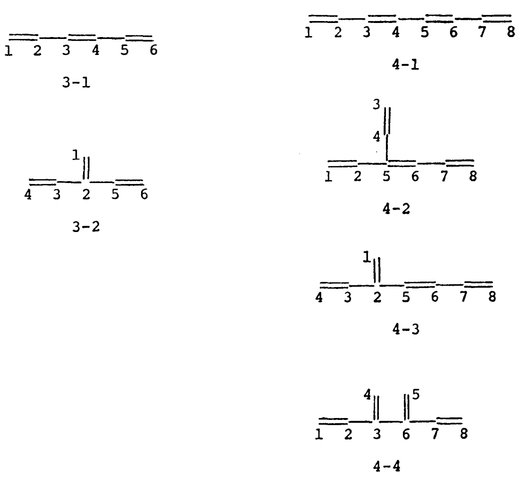


Chart 1.

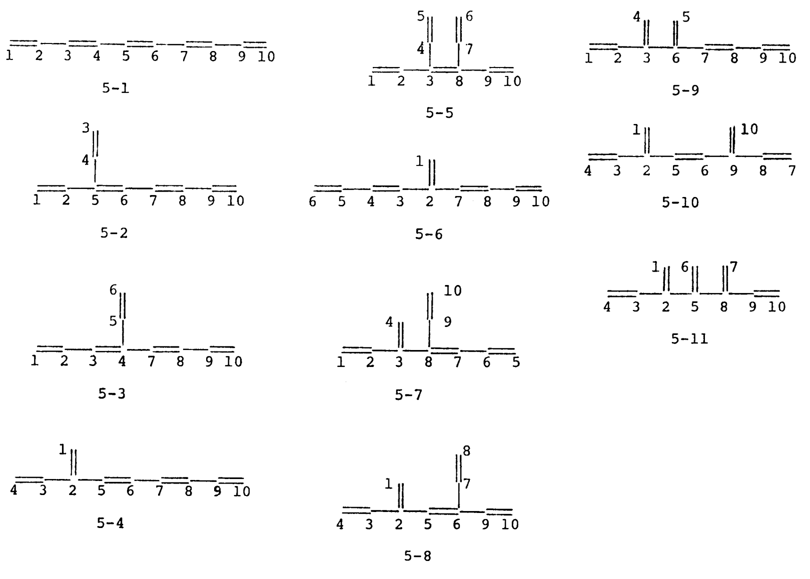


Chart 2.

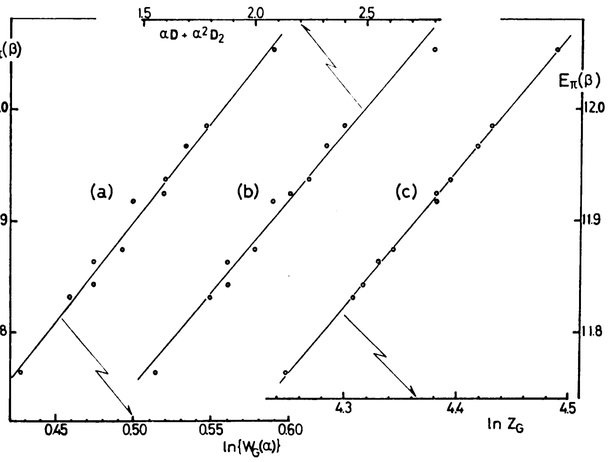


Fig. 5. Dependence of the E_π value of the decapentaene isomers on the various topological quantities. See also Table 5.
(a) Eq. 23, (b) Eq. 25, (c) Eq. 19.

first and second excited structures as

$$E_\pi \approx D + 0.2D_2. \qquad (25)$$

This is also an unexpectedly good correlation, if one knows that the numbers of the Dewar structures for decapentaene and dodecahexaene isomers are, respectively, around 20 and 10% of the total number of the resonance structures.

In order to clarify the secret of this fortuitous result, the distributions of the $w(G,j)$ coefficients of the Wheland polynomial for the following six typical series of branched polyenes were studied (see Chart 3 and Table 6).

In Fig. 6 are plotted the $w(G,j)$ and $w(G,j)\alpha^j$ values against j for linear polyene 14 and one of its isomers. Although both the two curves of the isomer shift a little toward larger j values, the overall shapes are simulated fairly well by Gaussian functions. Both the $w(G,j)$ and $p(G,n-j)$ values for an isomer with n double bonds in each series studied are expressed by

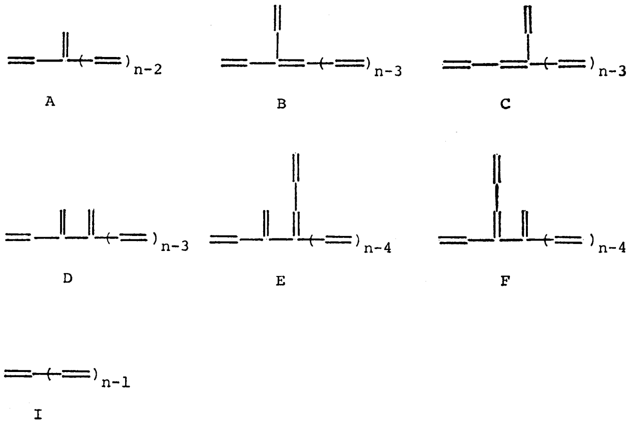


Chart 3.

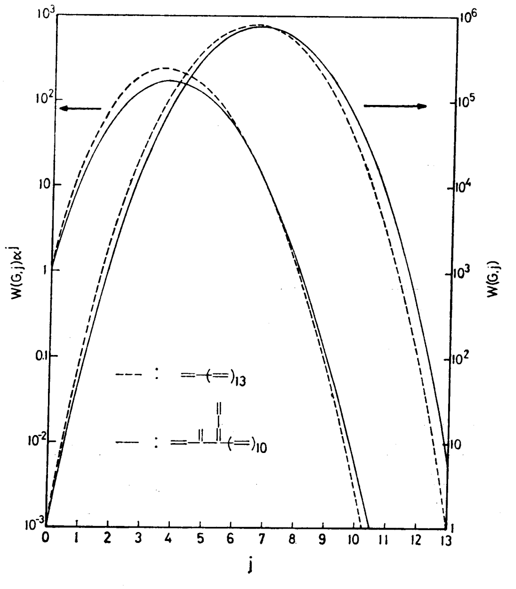


Fig. 6. Similar behaviors of $w(G,j)$ and $w(G,j)\alpha^j$ against j for $C_{28}H_{30}$ and one of its isomer.

TABLE 6. GENERAL EXPRESSIONS FOR THE COEFFICIENTS OF WHELAND POLYNOMIAL AND THE NON-ADJACENT NUMBERS FOR VARIOUS SERIES OF BRANCHED ACYCLIC GRAPHS

Series	j	$w(\mathrm{G},j)$	$p(\mathrm{G},n-j)$	$\Delta p(\mathrm{G},n-j)$
I	1	$\frac{1}{2}n(n-1)$	$\frac{1}{2}n(n+1)$	0
	2	$\frac{1}{12}n(n-1)^2(n-2)$	$\frac{1}{24}(n-1)n(n+1)(n+2)$	0
	3	$\frac{1}{144}n(n-1)^2(n-2)^2(n-3)$	$\frac{1}{720}(n-2)(n-1)n(n+1)(n+2)(n+3)$	0
A	1	$\frac{1}{2}(n^2-3n+4)$	$\frac{1}{2}(n^2-n+4)$	0
	2	$\frac{1}{12}(n-2)(n^3-6n^2+29n-36)$	$\frac{1}{24}(n-1)(n^3-n^2+22n-24)$	$\frac{1}{2}(n-2)$
	3	$\frac{1}{144}(n-2)(n-3)(n-4)(n^3-6n^2+59n-78)$	$\frac{1}{720}n(n-1)(n-2)(n^3+53n-66)$	$\frac{1}{10}(n-1)(n-2)(n-3)$
B	1	$\frac{1}{2}(n+1)(n-2)$	$\frac{1}{2}(n-1)(n+2)$	0
	2	$\frac{1}{12}(n^4-4n^3-7n^2+58n-60)$	$\frac{1}{24}(n^4+2n^3-13n^2+58n-72)$	$\frac{1}{2}(n-2)$
	3	$\frac{1}{144}(n-2)(n-3)\times(n^4-4n^3-25n^2+220n-264)$	$\frac{1}{720}(n-2)(n-1)\times(n^4+6n^3-19n^2+216n-360)$	$\frac{1}{10}(n-1)(n-2)(n-3)$
C	1	$\frac{1}{2}(n^2-3n+6)$	$\frac{1}{2}(n^2-n+6)$	0
	2	$\frac{1}{12}(n^4-8n^3+53n^2-202n+276)$	$\frac{1}{24}(n^4-2n^3+35n^2-130n+168)$	$(n-3)$
	3	$\frac{1}{144}(n-3)(n^5-12n^4+133n^3-1026n^2+3808n-4848)$	$\frac{1}{720}(n-2)(n^5-n^4+83n^3-479n^2+1476n-1800)$	$\frac{1}{5}(n-1)(n-3)^2$
D	1	$\frac{1}{2}(n^2-5n+10)$	$\frac{1}{2}(n^2-3n+10)$	0
	2	$\frac{1}{12}(n-2)(n^3-10n^2+63n-102)$	$\frac{1}{24}(n^4-6n^3+59n^2-174n+192)$	$\frac{1}{4}(n^2-5n+8)$
	3	$\frac{1}{144}(n-2)(n-3)(n^4-16n^3+173n^2-734n+1008)$	$\frac{1}{720}(n-2)(n^5-7n^4+131n^3-593n^2+1548n-1800)$	$\frac{1}{40}(n-2)(n-3)(n^2-5n+16)$
E	1	$\frac{1}{2}(n^2-5n+12)$	$\frac{1}{2}(n^2-3n+12)$	0
	2	$\frac{1}{12}(n^4-12n^3+89n^2-294n+360)$	$\frac{1}{24}(n^4-6n^3+71n^2-282n+456)$	$\frac{1}{2}(n^2-7n+14)$
	3	$\frac{1}{144}(n-4)(n-3)(n^4-14n^3+161n^2-688n+1404)$	$\frac{1}{720}(n^6-9n^5+175n^4-1395n^3+6664n^2-18396n+21600)$	$\frac{1}{20}(n^4-14n^3+89n^2-280n+348)$
F	1	$\frac{1}{2}(n^2-7n+22)$	$\frac{1}{2}(n^2-5n+22)$	0
	2	$\frac{1}{12}(n^4-16n^3+161n^2-662n+900)$	$\frac{1}{24}(n^4-10n^3+131n^2-578n+936)$	$\frac{1}{2}(n^2-7n+14)$
	3	$\frac{1}{144}(n-3)(n^5-24n^4+397n^3-3150n^2+11320n-14736)$	$\frac{1}{720}(n^6-15n^5+325n^4-2865n^3+13714n^2-34920n+36720)$	$\frac{1}{20}(n^4-14n^3+89n^2-280n+348)$

polynomials of n with order $2j$. The results for smaller j values are given in Table 6. All these results confirm that the values of $w(\mathrm{G},j)$ and $w(\mathrm{G},j)\alpha^j$ for the isomers behave quite similarly with those for the linear polyene.

Try to expand the function below

$$\begin{aligned}\left(1+\frac{w_1\alpha}{n}\right)^n &= 1 + w_1\alpha + \binom{n}{2}\left(\frac{w_1\alpha}{n}\right)^2 + \binom{n}{3}\left(\frac{w_1\alpha}{n}\right)^3 + \cdots \\ &= 1 + w_1\alpha + \frac{n-1}{2n}\cdot w_1{}^2\alpha^2 \\ &\quad + \frac{(n-1)(n-2)}{6n^2}\cdot w_1{}^3\alpha^3 + \cdots \\ &= \sum_{j=0} A_j\alpha^j, \end{aligned} \tag{26}$$

where w_1 is $w(\bar{n},1)$, or the number of the Dewar structures of linear polyene $\bar{n}$. Note that the coefficient A_j to α^j is proportional to $w_1{}^j$ or to the $2j$-th power of n. Compare this expansion with the Wheland polynomial for $\bar{n}$ as

$$W_{\bar{n}}(\alpha) = \sum_{j=0} w(\bar{n},j)\alpha^j, \tag{27}$$

whose coefficient $w(\bar{n},j)$ is also proportional to the $2j$-th power of n (see Eq. 2). Owing to the small value of α, $W_{\bar{n}}(\alpha)$ can be approximated, though not accurately but reasonably well, as expression 26, namely,

$$W_{\bar{n}}(\alpha) \sim \left(1+\frac{w_1\alpha}{n}\right)^n. \tag{28}$$

As inferred from the behavior of $w(\mathrm{G},j)$ observed above, we may also assume

$$W_{\mathrm{G}}(\alpha) \approx \left(1+\frac{w_1'\alpha}{n}\right)^n \tag{29}$$

for an isomer G with $w_1'=w(\mathrm{G},1)$. Then from Eq. 23 one gets

$$\begin{aligned}\Delta E_\pi &= E_\pi(\bar{n}) - E_\pi(\mathrm{G}) \\ &\approx \ln\{W_{\bar{n}}(\alpha)/W_{\mathrm{G}}(\alpha)\} \\ &\approx n\ln\left\{\left(1+\frac{w_1\alpha}{n}\right)\Big/\left(1+\frac{w_1'\alpha}{n}\right)\right\}.\end{aligned} \tag{30}$$

Since w_1 is equal to $n(n-1)/2$ (from Eq. 2), the value $w_1\alpha/n$ is smaller than unity for small n. Then ΔE_π can be approximated as

$$\Delta E_\pi \approx \alpha(w_1-w_1'). \tag{31}$$

This is a partial proof of relation 25. For larger n, however, the expression 31 would no longer be a good expansion of ΔE_π. In this case one has to expand $W_{\mathrm{G}}(\alpha)$ by the inclusion of higher $w(\mathrm{G},j)$ terms. This means that the larger the molecule the larger the weight of higher excited structures. However, for a group of moderate size of acyclic polyenes, the number of the Dewar structures is thus shown to be a good measure of the π-electronic energy.

Next the relation between $w(\mathrm{G},j)$ and $p(\mathrm{G},n-k)$ was studied. For $j,k\leq 1$ the results are the same as the case of linear polyenes. Namely, for polyene G with n double bonds,

$$K = w(\mathrm{G},0) = p(\mathrm{G},n) \tag{14'}$$

and

$$D = w(\mathrm{G},1) = p(\mathrm{G},n-1) - np(\mathrm{G},n). \tag{15'}$$

However, for larger values of j and k small correction should be introduced into relations 12 and 13.

Relation 14′ is guaranteed by definition. Relation 15′ has already been presented without proof by one of the present authors.[3,22] Since an acyclic polyene is an alternant hydrocarbon, namely, the corresponding graph is bipartite, the carbon atoms are grouped into starred and unstarred so that all the bonds are formed between atoms of different groups. As will be exemplified in Appendix, all the ineffective bonds in an excited canonical structure are also formed between atoms of different groups.

Suppose the C–C single bond skeleton of polyene G with n double bonds and choose $n-1$ disjoint bonds on which double bonds are to be drawn. There are $p(\mathrm{C},n-1)$ different ways. Since each double bond is so chosen as to span a couple of starred and unstarred atoms, there are left a couple of starred and unstarred atoms. Irrespective of the situation that they may or may not be adjacent, join them to form the n-th π bond. The resultant $p(\mathrm{G},n-1)$ graphs are the candidates for the set of the first excited canonical structures, or Dewar structures. It is obvious that no other candidate is possible. If the n-th π bond is formed between two adjacent atoms, the resultant graph is nothing else but the unexcited Kekulé structure to be deleted from the counting of $w(\mathrm{G},1)$ or D, and there are n such possible ways for each Kekulé structure. This completes the proof of Eq. 15′. Note that this relation is valid even for a graph with more than one Kekulé structures.

Let the difference between the right and left hand sides of Eq. 12 be defined as

$$\Delta p(\mathrm{G},n-k) = p(\mathrm{G},n-k) - \frac{k!(k+1)!}{(2k)!}\sum_{j=0}^{k}\binom{n-j}{k-j}w(\mathrm{G},j) \tag{32}$$

which was shown to be always positive for $k\geq 2$ of all the series studied. In Table 6 are given the general expressions of the $\Delta p(\mathrm{G},n-2)$ and $\Delta p(\mathrm{G},n-3)$ for each series. It is seen from the expression of $p(\mathrm{G},n-k)$ and $\Delta p(\mathrm{G},n-k)$ that the relative correction is at most in the order of n^{-2} and negligible for larger polyenes. This is also the case with the higher values of k. Thus the number of the higher excited structures can be approximated by Eq. 13 for branched polyenes in terms of the set of the $p(\mathrm{G},k)$ numbers, which can systematically be obtained by the use of several recursion formulas.[14,23]

It is worth mentioning here that the quantities independently obtained from VB and GT are thus found to be closely related with each other through the quantity of MO. Work in these lines is in progress for the mathematical properties of the number of the resonance structures of polycyclic hydrocarbons.

Appendix

A Note on the Numbering of Atoms for Acyclic Polyenes. At present we are not yet in a position to state the unambiguous method for numbering the atoms to generate the Wheland polynominal of the highest priority for an arbitrary acyclic polyene. However, our experience on a number of examples has led to several empirical rules for the numbering of a polyene with a few branches.

Consider first the mapping procedure for generating the

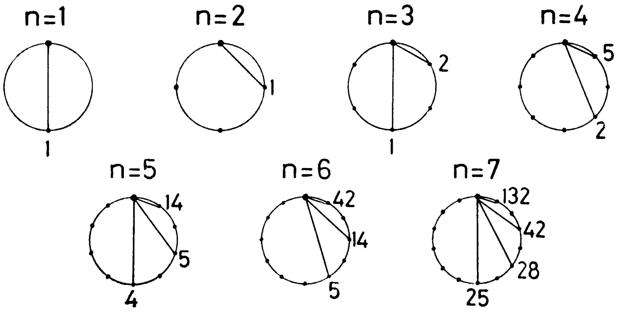


Fig. 7. Distribution of the numbers of the effective and ineffective bonds spanning from a pivot point among a set of C_n standard patterns. No bond is found between a pair of atoms of the same parity, and the distribution is symmetrical.

Wheland polynomial exemplified in Fig. 1. Draw $C_n=(2n)!/\{n!(n+1)!\}$ standard patterns for the set of circularly arranged and numbered $2n(=N)$ points. In each pattern n noncrossing lines are drawn. Choose a point as the pivot from the $2n$ points. Then for each member of the $2n-1$ points count the number of patterns in which it is connected with the pivot point. The results for smaller n's are shown in Fig. 7. Observe that no line is drawn between a pair of points of the same parity. Namely, an alternant hydrocarbon has no bond between a pair of starred atoms and also between a pair of unstarred atoms. The number of the effective bonds are the largest, and the number of the ineffective bonds rapidly decreases with the increase of the length. The sum of these numbers is C_n.

Recall that the set of the canonical resonance structures are obtained by mapping the given arbitrary numbered graph G (or the π-electron skeleton) onto each of the C_n standard patterns. The degree of excitation j for a resonance structure is the number of the ineffective bonds and $w(\mathrm{G}, j)$ is the number of j-th excited structures for G. Then the total number of the effective bonds J in the set of the C_n resonance structures is given by

$$J = n\cdot C_n - \sum_{j=1} j\cdot w(\mathrm{G},j).$$

Note that the summation in the second term is equal to $W_\mathrm{G}'(1)=(\mathrm{d}W_\mathrm{G}(x)/\mathrm{d}x)_{x=1}$, where $W_\mathrm{G}(x)$ is the Wheland polynomial $W_\mathrm{G}(x)=\sum_{j=0} w(\mathrm{G}, j)\cdot x^j$. The highest priority is given to such a $W_\mathrm{G}(x)$ expression that has the top-heaviest set of the coefficients, which we are going to search. It is not sufficient but necessary for that expression to have the largest J value, or the smallest $W_\mathrm{G}'(1)$ value.

For convenience's sake let us define the term "number difference", $d_{ij}=\min(|i-j|, 2n-|i-j|)$, for a pair of atoms i and j forming a bond. All the bonds are then classified into the following three types according to their d_{ij} value as,

$$\alpha\text{-type with } d_{ij} = 1$$

$$\beta\text{-type with } d_{ij} = 2, 4, 6, \cdots$$

$$\gamma\text{-type with } d_{ij} = 3, 5, 7, \cdots$$

Unless confusion may occur α, β, and γ stand also for the numbers of the bonds of the corresponding types. Then all the above observations and discussions lead to the following recipes for the numbering of atoms so as to give the largest J value, or the smallest $W_\mathrm{G}'(1)$ value.

(1) Every bond should be composed of a pair of atoms of different parity, or $\beta=0$.

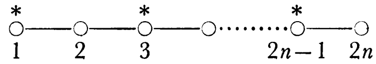
(2) The number of γ-type bonds should be minimized. There are several possible ways for satisfying the conditions (1) and (2). In these cases recipe (3) would be applied.

(3) The sum $D=\sum_{i<j} d_{ij}$ of the "number difference" for all the bonds should be minimized. Further, to the case where several numberings are still possible in which recipes (1)—(3) are obeyed we may apply.

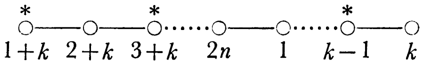
(4) The sizes of the polyene fragments obtained by excising the γ-(and also β-) type bonds should be as uniform as possible.

However, (3) and (4) should not necessarily be obeyed, and their relative priority seems to change from case to case.

Linear Polyene. Application of recipes (1) and (2) to a linear polyene assures that the following numbering gives the Wheland polynomial of the highest priority,



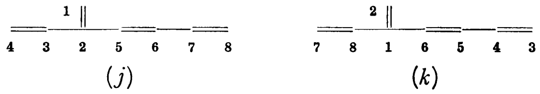
The cyclic change of numbering as



$(0<k<2n)$

gives the same result.

Polyene with One Branch. Three carbon chains, P_1, P_2, and P_3, emanate, from the carbon atom as the junction of the polyene with one branch, where P_1 is an odd chain, P_2 a shorter even chain, and P_3 longer even chain. Application of recipes (1) and (2) gives the numbering as shown in Chart 4a. For graph 4-3 in Chart 1 the following two numberings give the same result,



since they are related to each other by the formula

$$j + k = l \text{ or } l + 2n,$$

where j and k are the numberings given to the same atoms, respectively, by the numbering systems (j) and (k), and l is an arbitrary integer (here $l=3$).

Polyene with Two Branches. Consider first those polyenes with two branches, which are separated by one bond. There

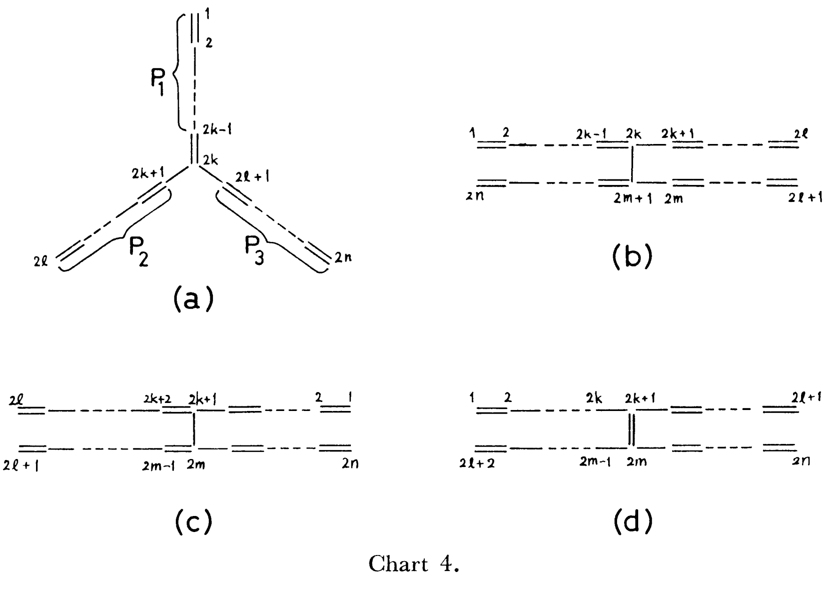
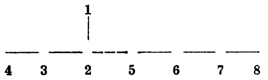
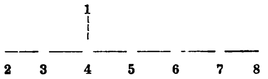
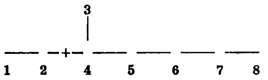
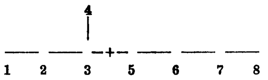


Chart 4.

Table 7. An example showing the factors for determining the coefficients of the Wheland polynomial

Numbering[a)]	$W_G(x)$	$W_G'(1)$	β[b)]	γ[c)]	Fragment[d)]
	$1+4x+8x^2+x^4$	24	0	1	4+4
	$1+4x+7x^2+2x^3$	24	0	1	1+7
	$1+3x+7x^2+3x^3$	26	1	0	2+6
	$1+2x+10x^2+x^4$	26	1	0	4+4

a) —— : α-type bond, –+– : β-type bond, ––– : γ-type bond. b) Number of the β-type bond. c) Number of the γ-type bond. d) Indicates the sizes of the polyene chains obtained by excising the β- and γ-bonds.

are two cases depending that the central bond is single or double. For the former case the two numberings in Charts 4b and c are the candidates for the highest priority. Then compare the number differences at the central bridge bond, and the numbering giving the smaller value is chosen as the best.

In the case of the polyene with a central bridge double bond, the numbering with the highest priority can be chosen as the one having the smallest number difference at the bridge from the possible numberings of the types as in Chart 4d.

Table 7 shows how the Wheland polynomial depends on the recipes for the numbering given above.

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16) This algorithm is indeed time-consuming for larger graph even with a computer, since the time required for the enumeration inceases with the factorial of the number of points in the graph.

17) The series C_n of the numbers 1, 2, 5, 14, 42, ···, thus derived, are known as the Catalan numbers.

18) By the use of a HITAC 8700/8800 computer of the University of Tokyo, it took 10 s for the graph with 20 points below which the machine time is negligible. However, as the machine time increases exponentially in this region, an estimated time for a graph with 30 points would be 1.5 h.

19) Note that this notation differs from what was used by one of the present authors elsewhere.[14)] In this paper all the molecules have even number of carbon atoms.

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