

Graph theory and molecular orbitals. XII. Acyclic polyenes

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A graph-theoretical study of acyclic polyenes is carried out with an emphasis on the influence of branching on several molecular properties. A definition of branching is given and several branching indices are analyzed. The case of polyenes without a Kekulé structure is discussed briefly. The main conclusions are: (a) thermodynamic stability of conjugated polyenes decreases with branching, but (b) reactivity, in general, increases with branching.

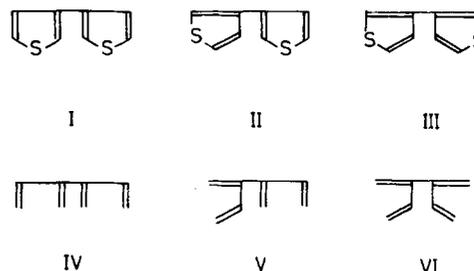
I. INTRODUCTION

In the present series of papers^{1,2} several topological properties of conjugated compounds^{3,4} have been analyzed using a graph-theoretical approach⁵ and a number of known chemical rules could be confirmed and/or justified in this way. Some other regularities usually regarded as very general ones are shown to be of restricted validity (see, e.g., Part VII of this series). Finally, the insight which graph theory gives into the structural relationships of the δ -bond network of a conjugated system enables the formulation and prediction of many previously unknown phenomena (see especially Parts III and VI), some of which have since been confirmed experimentally.^{6,7} These topological studies are, however, very complex because every topological property is determined by a variety of different structural details of the molecular graph, which are usually present simultaneously. Therefore, it is sometimes a rather difficult task to deduce what is actually the effect of one particular structural detail on a given topological property. For example, it has been demonstrated⁸ that total π -electron energy is mainly determined by the number of vertices and edges. However, since not energies but rather energy differences are important in chemistry, other topological factors, which make only small contributions to the energy, become dominant in determining chemical behavior. These factors seem to be the ring size (see Parts III and V and Ref. 9), the number of Kekulé structures (Part X), and branching of the carbon atom skeleton. While the first two of these factors have been now extensively investigated, the effect of the third is almost completely unknown. The reason for this is, probably, that almost all polycyclic molecules which have been studied so far are branched in a similar way so that this effect has been largely obscured.

In order to investigate the effect of branching on topological properties, a special class of conjugated systems has been chosen—the acyclic polyenes. These compounds have no rings and thus all complicated ring effects are eliminated; besides if one considers only acyclic polyenes with a given number N of carbon atoms, the number of carbon-carbon bonds ν is constant ($\nu = N - 1$). Moreover, the number of Kekulé structures K is either one or zero and in practice we are normally interested only in molecules having $K = 1$. Thus in the case of acyclic polyenes it is possible to keep all topological factors, except branching, constant. However, the conclusions obtained in this paper are valid not only for acyclic polyenes, but for the general polycyclic case

as well. We hope that the present study gives information useful for predicting topological properties of all conjugated systems.

As an additional reason for the investigation of acyclic systems we mention the graphical study of heterocyclic compounds.¹⁰ It has been demonstrated¹⁰ that the relative stabilities of isomeric heterocyclic compounds containing δ -bivalent atoms (\ddot{S} , \ddot{O} , $\ddot{N}H$) can be deduced from the knowledge of the stabilities of the conjugated hydrocarbons obtained after the deletion of all heteroatoms. Thus, for instance,¹¹ the stability differences between I, II, and III parallel the differences between IV, V, and VI.



II. TREE GRAPHS

In this section we give a short survey of properties of acyclic graphs which are in graph theory⁵ called "trees." Of course, the molecular graph⁴ of an acyclic polyene is a tree. We also give here the necessary graph-theoretical definitions.

The molecular graph is necessarily connected and therefore

$$\nu = N - 1, \quad (1)$$

where N and ν denote the number of vertices and edges. For obvious reasons the case of even N will be considered only; it is convenient to let $n = N/2$.

The number of vertices which are adjacent to a vertex p is called the "degree" of the vertex p and is denoted by D_p . Note that

$$\sum_{p=1}^N D_p = 2\nu. \quad (2)$$

In graphs associated with conjugated systems the following inequality always holds¹²:

$$D_p \leq 3. \quad (3)$$

Let P , S , and T denote the number of vertices having D_p equal to 1, 2, and 3, respectively. Then

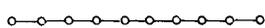
$$P + S + T = N \quad (4)$$

$$P + 2S + 3T = 2\nu. \quad (5)$$

Combining Eqs. (1), (4), and (5) one obtains for trees

$$T = P - 2. \quad (6)$$

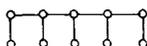
The tree with minimal T and maximal S values is called a "chain." Intuitively, a chain is nonbranched. By increasing the value of T , branching intuitively should increase also. It can be proved that the molecular tree with maximal T and minimal S values which has the Kekulé graph⁴ is the "comb." Hence, intuitively, the comb is the most branched molecular tree with a single Kekulé graph. Graphs VII and VIII are the chain and the comb with ten vertices.



L_{10}

$$P=2, S=N-2, T=0$$

VII



C_{10}

$$P=n, S=2, T=n-2$$

VIII

However, a more precise definition of branching will be given in Sec. IV.

Tree graphs are bipartite,¹³ i.e., the corresponding hydrocarbons are alternant.

The number of Kekulé graphs K in trees is either one or zero. Moreover

$$\det A = (-1)^n K, \quad (7)$$

where A is the adjacency matrix⁴ of the corresponding graph.

In chemical studies of unsaturated molecules the spectrum of the graph⁴ is of particular importance. We denote the set of eigenvalues of A (that is to say the graph spectrum) by x_1, x_2, \dots, x_n and adopt the convention

$$x_1 \geq x_2 \geq \dots \geq x_n. \quad (8)$$

The corresponding eigenvectors are labelled with C_t ($t=1, 2, \dots, N$). Hence

$$A C_t = x_t C_t. \quad (9)$$

The graph spectrum is therefore the set of the roots of the characteristic polynomial⁴ $P(G, x)$

$$P(G, x) = \det(A - xI), \quad (10)$$

where I is a unit matrix and G denotes the corresponding graph.

It is well known¹⁴ that the eigenvectors and eigenvalues of the molecular graph are closely related to the Hückel molecular orbitals and corresponding energy levels. In this study of particular interest are C_1 —the lowest occupied molecular orbital (LOMO), and, for cases when $x_n \neq 0$, C_n —the highest occupied

and C_{n+1} —the lowest unoccupied molecular orbitals (HOMO and LUMO). The corresponding energies (including the total energy) will be expressed in β units.

As a consequence¹⁵ of Eq. (3)

$$-3 < x_t < 3 \quad (11)$$

for all t . Since trees are bipartite, the graph spectrum is symmetric,⁴ i.e.,

$$x_t + x_{N-t+1} = 0, \quad (12)$$

for $t=1, 2, \dots, n$. Because of Eq. (7), $x_n = x_{n+1} = 0$ if, and only if $K=0$. The difference $x_n - x_{n+1} = 2x_n$ has been called "the HOMO-LUMO separation"¹⁶ and will be denoted here by Δ .

The total π -electron energy E_π is given by

$$\alpha N + \beta 2 \sum_{t=1}^n x_t$$

but for the purposes of the present investigation only the quantity

$$E_\pi = 2 \sum_{t=1}^n x_t \quad (13)$$

has to be discussed.

III. THE ROLE OF THE KEKULÉ STRUCTURES

Acyclic polyenes have either one Kekulé structure ($K=1$) or have none ($K=0$). In this latter case the HOMO-LUMO separation Δ is zero and is accompanied by a triplet ground state and extremely high chemical reactivity.¹⁷ In fact, conjugated hydrocarbons without a Kekulé structure have never been isolated.¹⁸ From Eq. (7) it follows that if a polyene has a Kekulé structure, the HOMO-LUMO separation is not zero and a singlet ground state is to be expected. Therefore, for acyclic polyenes with $K=1$ Hückel theory (as well as various more sophisticated SCF MO theories)¹⁹ predicts a polyolefinic chemical behavior. We would summarize these well known facts as: *acyclic polyenes with $K=0$ are much more reactive (that is kinetically unstable) than those with $K=1$.*

The dependence of thermodynamic stability on K is less simple. Some results in this direction derived in Part X show that structures with $K=0$ are usually thermodynamically less stable than those with $K>0$. However, this is not a general rule, as will be pointed out later.

In order to obtain some insight into the role which a Kekulé structure plays in determining E_π , two model graphs have been investigated—the chain L_N (IX) and the snake S_N (X).



L_N

IX



S_N

X

The index N denotes the number of vertices (which is even). Of course, $K=1$ for the chain and $K=0$ for the

snake. Note that total π -electron energy is shown²⁰ to be in a simple linear correlation with the measurable thermodynamic quantities (heats of formation, enthalpy, etc.).

Now, the characteristic polynomial of the chain graph L_N fulfills the recurrence relation²¹

$$P(L_N, x) = x P(L_{N-1}, x) - P(L_{N-2}, x). \quad (14)$$

If one introduces

$$x = 2 \cos y \quad (15)$$

it can be shown that

$$P(L_N, x) = \sin(N+1)y / \sin y. \quad (16)$$

From (16) it follows immediately that

$$x_t = 2 \cos[t\pi/(N+1)], \quad (17)$$

for $t=1, 2, \dots, N$. The total π -electron energy is then²²

$$E_r(L_N) = 2 \csc[\pi/2(N+1)] - 2. \quad (18)$$

The characteristic polynomial of the snake graph S_N fulfills the recurrence relation²¹

$$P(S_N, x) = x P(L_{N-1}, x) - x P(L_{N-2}, x) \quad (19)$$

and if Eqs. (15) and (16) are used,

$$P(S_N, x) = 4 \operatorname{csc} y \cos(N-1)y \quad (20)$$

Therefore the spectrum of S_N is

$$x_t = 2 \cos \frac{(2t-1)\pi}{2(N-1)}, \quad t=1, 2, \dots, n$$

$$x_{n+1} = 0, \quad (21)$$

$$x_t = 2 \cos \frac{(2t-3)\pi}{2(N-1)}, \quad t=n+2, \dots, N$$

and

$$E_r(S_N) = 2 \cot[\pi/2(N-1)]. \quad (22)$$

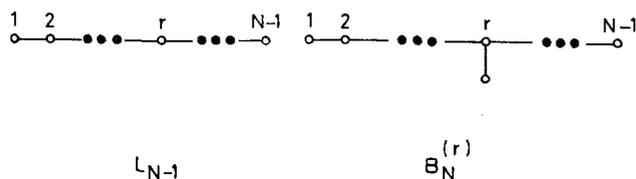
For sufficiently large N ,

$$E_r(L_N) \approx (4/\pi)N + (4/\pi) - 2 \quad (23)$$

$$E_r(S_N) \approx (4/\pi)N - (4/\pi) \quad (24)$$

which means that the snake is less stable than the chain by approximately $8/\pi - 2 = 0.546\beta$. This destabilization can be ascribed mainly to the absence of a Kekulé structure for S_N .

The graphs L_N and S_N can be viewed as though they had been obtained by joining an isolated vertex to the graph L_{N-1} (XI) at the position 1 and 2, respectively. This leads to the problem of the energy of the graph $B_N^{(r)}$ (XII) obtained by joining a vertex to the L_{N-1} at the



XI

XII

position r . Of course, $B_N^{(1)} = L_N$ and $B_N^{(2)} = S_N$. This problem cannot be solved analytically in the general case and therefore a first order perturbational approach has been used. Thus,

$$E_r(B_N^{(r)}) - E_r(L_{N-1}) \approx \delta E_N^{(r)} = \sum_{j=1}^{N/2} \frac{2}{N+1} \frac{\sin^2[rj\pi/(N+1)]}{2 \cos[j\pi/(N+1)]}. \quad (25)$$

Because

$$\frac{\sin^2 r\theta}{\cos\theta} = \frac{\sin^2(r-2)\theta}{\cos\theta} - \cos(2r-1)\theta + \cos(2r-3)\theta \quad (26)$$

the following relation holds:

$$\delta E_N^{(r)} = \delta E_N^{(r-2)} + \frac{(-1)^r}{2(N+1)} \left[\csc \frac{(2r-3)\pi}{2(N+1)} + \csc \frac{(2r-1)\pi}{2(N+1)} \right] \quad (27)$$

and for $r/N \ll 1$,

$$\delta E_N^{(r)} = \delta E_N^{(r-2)} + (-1)^r \frac{4}{\pi} \frac{r-1}{(2r-1)(2r-3)}. \quad (28)$$

Since $\delta E_N^{(1)}$ and $\delta E_N^{(2)}$ are known [see Eq. (18) and (22)], all other $\delta E_N^{(r)}$'s can be calculated from Eq. (27). Analysis shows that for odd r (the case of $K=1$) $\delta E_N^{(r)}$ decreases monotonically and rapidly converges to a constant value as r increases. Similarly, for even r (the case of $K=0$), $\delta E_N^{(r)}$ increases monotonically and also converges rapidly. This is illustrated in Fig. 1.

The result of the above discussion and those presented in Fig. 1 show that total π -electron energy of acyclic polyenes exhibits a small sensitivity to the position of the branched atom provided that the number of Kekulé structures is constant. Branching at the termini of the chain has the largest effect for both the cases of $K=1$ and $K=0$.

From now on we restrict ourselves to polyenes having $K=1$ because here we are not interested in effects caused by the change of K (this latter problem was discussed in more details in Part X). This restriction will enable the study of just one topological parameter—the branching.

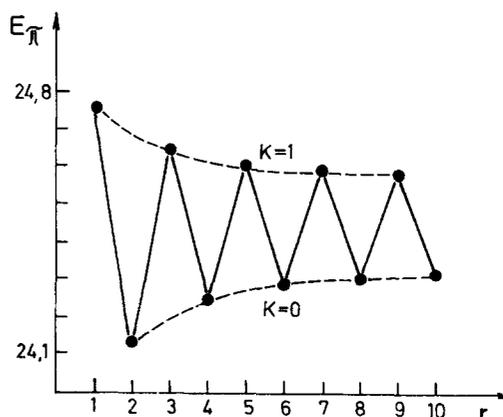
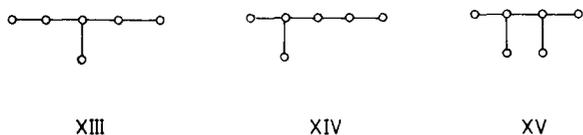


FIG. 1. π -electron energy of $B_{20}^{(r)}$.

IV. BRANCHING AND ITS MEASURES

In order to determine what is meant by branching it is natural to start with the "intuitively obvious" facts that for some pairs of tree graphs it is possible to decide unambiguously which of them is more branched. It is our belief that only trees with equal number of vertices can be compared meaningfully. Consequently, the subsequent discussion will always be restricted to classes of trees with the same N value.

The least branched tree is, of course, the chain, while the most branched one would be the "star." (A star graph with $m+1$ vertices has m vertices of degree one and a vertex of degree m ; therefore such graphs are not important in chemical studies.) Whereas the statement that the graphs XIII and XIV are less branched than the graph XV is completely acceptable, the question whether XIII or XIV is more branched necessarily leads to unproductive academic discussions. This latter question is, moreover, meaningless, since it requires a measure for branching which one first needs to define.



Let us consider a class of (tree) graphs. For certain pairs of these graphs one can decide which of them is more branched. If to every graph G_j from the class, according to a given recipe, a number Γ_j can be associated such that $\Gamma_j > \Gamma_k$ in all cases where one can decide that G_j is more branched than G_k , then we call Γ a *measure of branching*. In particular, for trees which fulfill the relation (3), that is for chemically relevant tree graphs, a measure of branching should have the property

$$\Gamma_j > \Gamma_k \text{ if } T(G_j) > T(G_k). \quad (29)$$

There exist many pairs of similarly branched graphs for which both $\Gamma_j > \Gamma_k$ and $\Gamma_k > \Gamma_j$ would suffice and it is clear that the choice of the measure of branching is to a great extent arbitrary.

Much work has been done in the last twenty years in an effort to correlate numerous thermodynamical properties (mainly of saturated hydrocarbons) with some measure of branching.^{23,24} A number of measures (often called "indices") has been proposed and usually it was possible to demonstrate a satisfactory correlation between the measured quantities and the proposed index. Instead of defining a new measure, we would like here just to point out that such measures are all mutually closely correlated.

In Part III of this series it was shown that the following sums appear in a topological formula for total π energy

$$M_1 = \sum_{p=1}^N D_p^2 \quad (30)$$

$$M_2 = \sum_{(p,q)} D_p D_q, \quad (31)$$

where $\sum_{(p,q)}$ denotes summation over all edges in the graph. Recently²⁴ a similar index

$$M_R = \sum_{(p,q)} (D_p D_q)^{1/2} \quad (32)$$

has been proposed for characterization of molecular branching.

For molecular graphs

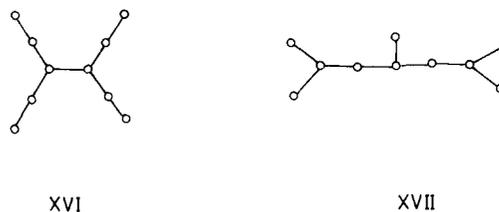
$$M_1 = 9T + 4S + P \quad (33)$$

and if Eqs. (1), (4), and (5) are used

$$M_1 = 4N - 6 + 2T. \quad (34)$$

Therefore M_1 will necessarily fulfill the demand (29), and can be used as a measure of branching. Besides, since the measure M_1 is completely determined by N and T , all molecular graphs with the same number of branchings (T) turn out to have the same M_1 values, regardless of other structural details. This seems to be an advantage because the problem of branching within a class of trees with fixed N and T is automatically avoided.

Numerical calculations show that the index M_2 deviates in many cases from the requirements of Eq. (29), and therefore cannot be used as a measure of branching. As examples consider the graphs XVI ($M_2 = 41$, $T = 2$) and XVII ($M_2 = 39$, $T = 3$).



All three indices M_1 , M_2 , and M_R were applied to the class of all 47 trees with nine and all 106 with ten vertices.²⁵ The numerical results obtained show that any of these indices orders these trees in approximately the same way. Moreover, there is a linear correlation between M_R and M_2 and a parabolic correlation between M_1 and M_2 . Thus a plot of the 47 M_R indices for trees with nine vertices vs the corresponding M_2 indices can be correlated by a line of the form $M_R - M_R^0 = 0.217 (M_2 - M_2^0)$ with a standard deviation of 0.244 in the values covering the range of M_R from 14.83 for the chain to 22.63 for the star. The values M_R^0 and M_2^0 refer to these indices for the chain. The slope was *not* obtained by least squares fitting but represents the result of forcing the line to pass through the points for the chain and the star. In spite of the rigidity of this approach, it can be seen that the correlation is fair.

When an additional degree of freedom is added by fitting these same data with a parabola (also constrained to pass through the points for the chain and the star), the standard deviation diminishes to 0.163 with a line of the form $M_R - M_R^0 = 0.190 (M_2 - M_2^0) + 0.00074 (M_2 - M_2^0)^2$. Application of a conventional statistical F test

indicates that the improvement is significant at better than the 99% confidence level. However, because of the smallness of the coefficient of the square term we feel that it is more useful to think of the correlation as essentially linear.

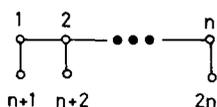
When the same treatment is applied to the 106 indices for the graphs with 10 vertices, very similar results are obtained. Thus the linear equation has a slope of 0.208 and a standard deviation of 0.236 while the parabolic equation has coefficients of 0.189 and 0.00039 with a standard deviation of 0.162. These results confirm the conclusion above that the correlation between M_R and M_2 is essentially linear. Although graphs with other N values have not been tested, we see no reason to believe that they would behave differently.

The situation is somewhat different with measures M_1 and M_2 . For the trees with nine vertices the linear correlation had a slope of 1.167 and a standard deviation of 5.08. With a parabolic fit the standard deviation was markedly reduced to 1.25 for the line $M_1 - M_1^0 = 0.451 (M_2 - M_2^0) + 0.0199 (M_2 - M_2^0)^2$. Here the square term is significant both statistically and practically. For the 106 graphs with 10 vertices a similar line $M_1 - M_1^0 = 0.457 (M_2 - M_2^0) + 0.0140 (M_2 - M_2^0)^2$ and a standard deviation of 1.28 were obtained.

Similar correlations also exist between other branching indices.²³ In the considerations which follow the measure M_1 is used, mainly because of the simplicity with which it can be evaluated. It should be emphasized once again that M_1 is chosen completely arbitrarily. The statistical analysis described above shows, however, that closely analogous, if not identical, results and conclusions would be obtained if some other measure would be used. Therefore, the choice of this particular measure is *irrelevant for the discussions which follow*. The topological rules discussed in Sec. VI are highly insensitive to the measure of branching used.

V. THE TWO EXTREME CASES

Before discussing some general regularities of the dependence of several properties on branching, it is instructive to compare the two extremely branched molecular graphs (having $K=1$)—the nonbranched chain (L_{2n}) and the maximally branched comb (C_{2n}). The spectrum of both graphs can be obtained in a closed analytical form. In fact, the spectrum of the comb is closely related to the spectrum of the chain. If the vertices of C_{2n} are labeled as indicated in XVIII



C_{2n}

XVIII

its adjacency matrix is of the form

$$A(C_{2n}) = \begin{bmatrix} A(L_n) & \mathbf{I} \\ \mathbf{I} & \mathbf{O} \end{bmatrix} \quad (35)$$

from which it follows properly that

$$P(C_{2n}, x) = x^n P(L_n, x - 1/x). \quad (36)$$

Now, because of Eq. (17),

$$P(L_n, z) = \prod_{t=1}^n \left(z - 2 \cos \frac{t\pi}{n+1} \right) \quad (36a)$$

it is

$$\begin{aligned} P(C_{2n}, x) &= x^n \prod_{t=1}^n \left(x - \frac{1}{x} - 2 \cos \frac{t\pi}{n+1} \right) \\ &= \prod_{t=1}^n \left(x^2 - 1 - 2x \cos \frac{t\pi}{n+1} \right) \end{aligned} \quad (37)$$

and, therefore, the spectrum of the comb with $2n$ vertices is

$$x_t = \cos \frac{t\pi}{n+1} + \left(1 + \cos^2 \frac{t\pi}{n+1} \right)^{1/2}, \quad t = 1, 2, \dots, n \quad (38)$$

$$x_{n+t} = \cos \frac{t\pi}{n+1} - \left(1 + \cos^2 \frac{t\pi}{n+1} \right)^{1/2}, \quad t = 1, 2, \dots, n.$$

The total π -electron energy is then

$$E_\pi = \sum_{t=1}^{2n} \left(1 + \cos^2 \frac{t\pi}{n+1} \right)^{1/2} \quad (39)$$

and for sufficiently large n

$$E_\pi \approx 2.432n - 0.396 \quad (40)$$

since²⁶

$$\frac{1}{\pi} \int_0^{2\pi} (1 + \cos^2 t)^{1/2} dt = 2.4301. \quad (41)$$

These analytical formulas enable the comparison of properties of the molecular graphs L_{2n} and C_{2n} in the general case. We will be mainly interested in the following three quantities—position of the LOMO level, HOMO–LUMO separation, and total π -electron energy.

(a) The two LOMO levels

$$x_1(L_{2n}) = 2 \cos[\pi/(2n+1)] \quad (42)$$

$$x_1(C_{2n}) = \cos \frac{\pi}{n+1} + \left(1 + \cos^2 \frac{\pi}{n+1} \right)^{1/2} \quad (43)$$

are increasing functions of n , but the LOMO of C_{2n} is always more stable than that of L_{2n} (except, of course, for $n=1$ and $n=2$), i.e.,

$$x_1(C_{2n}) > x_1(L_{2n}) \quad (44)$$

for $n > 2$. Moreover, the difference $x_1(C_{2n}) - x_1(L_{2n})$ increases with the increase of n showing that one should expect that, in general, branching will increase the value of x_1 .

(b) The HOMO–LUMO separations are

$$\Delta(L_{2n}) = 4 \sin[\pi/2(2n+1)] \quad (45)$$

$$\Delta(C_{2n}) = 2 \left[\left(1 + \cos^2 \frac{\pi}{n+1} \right)^{1/2} - \cos \frac{\pi}{n+1} \right]. \quad (46)$$

$\Delta(L_{2n})$ is a monotonically decreasing function of n , while $\Delta(C_{2n})$ is monotonically increasing. For large enough n (that is for $n \rightarrow \infty$):

$$\Delta(L) = 0 \quad (47)$$

$$\Delta(C) = 2(\sqrt{2} - 1) = 0.828. \quad (48)$$

Therefore, by increasing the number of atoms a linear polyene becomes more and more reactive. In contrast, the increase of the size of a "comblike" molecule should not be accompanied by increasing reactivity.

This completely different behavior of the HOMO-LUMO separation in the two classes of compounds can be ascribed to the increase in branching. One may, thus, expect that branching will in general increase Δ and thus that the more branched conjugated molecules are expected to be less reactive.

(c) Instead of comparing the total π -electron energies of these two classes of polyenes, it seems to be sufficient to analyze the mean energy $e_r = E_r/N$ for large N . Equations (23) and (40) are applicable for this case, and

$$e_r(L_{2n}) - e_r(C_{2n}) = (8/\pi - 2.432)/2 = 0.05724. \quad (49)$$

This result can be understood as meaning that every branch in C_N introduces a negative contribution to E_r of approximately $0.05724 \times 2 \approx 0.1\beta$. In Sec. VI this conclusion will be supported by additional numerical examples.

A curious fact that can be demonstrated by comparing Eqs. (24) and (40) is that for a sufficiently large N the π -electron energy of a "comblike" polyene should be less than the energy of the isomeric "snake-like" polyene. This means that *isomeric structures can be designed where the isomer with the larger number of Kekulé structures is thermodynamically less stable than the isomer with the smaller K value*. The snake S_{18} ($K=0$, $E_r = 21.6$) and the comb C_{18} ($K=1$, $E_r = 21.5$) are the smallest pair of molecular graphs having such an "anomalous" property.

The final conclusion of this analysis is that "comblike" polyenes should be thermodynamically less stable but kinetically more stable than their linear isomers. Thus, these molecules provide examples of conjugated systems where chemical stability does not parallel thermodynamical stability and where chemical behavior and thermodynamical behavior of a compound should be rigorously distinguished.

VI. RELATIONS BETWEEN SOME GRAPH-SPECTRAL PROPERTIES AND BRANCHING

In the preceding section the maximally and minimally branched graphs (with $K=1$) were studied. It is natural to expect that the properties of intermediately branched molecular graphs (with the same N and K values) will be somehow between these two extremes. Numerical calculations were performed for all possible molecular trees possessing a Kekulé graph and having $N=2, 4, 6, 8$, and 10 vertices. On Fig. 2 and Fig. 3 are plotted the values of x_1 and x_n vs T (that is M_1). The trend which is evident from these figures can be summarized as:

Rule 1: The LOMO level is stabilized with increased branching.

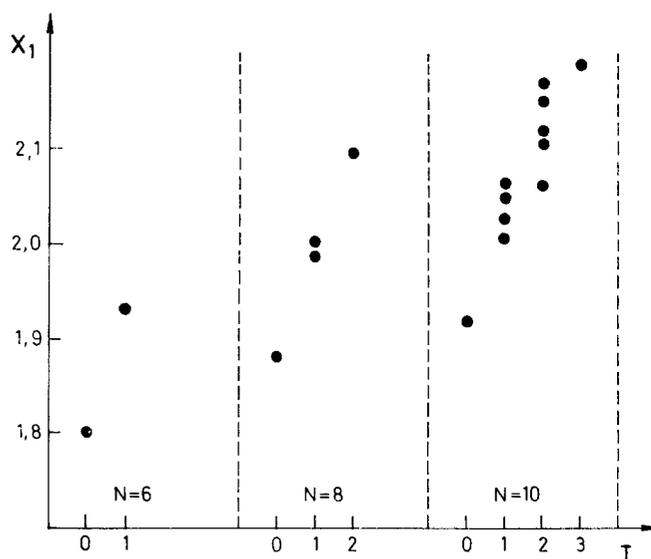


FIG. 2. The change of the LOMO level with branching.

Rule 2: The HOMO-LUMO separation increases with increased branching.

Both rules reflect only the general behavior of x_1 and x_n vs branching, and more or less important deviations could occur in particular cases. The comparison of Figs. 2 and 3 shows also that Rule 1 seems to be more precisely fulfilled, that is, violations from Rule 1 are much less severe than from Rule 2. With respect to this it is interesting that in an important mathematical paper Lovász and Pelikán²⁷ suggested that x_1 can be used as a measure of branching. They were able to prove that if all the trees with a given number of vertices are ordered in a sequence according to the increase of their x_1 value, the chain will have the first position (minimal x_1) while the star has the end position (maximal x_1) in the sequence. Moreover, the snake graph always has the second position and the graph XIX next position to the last.



XIX

Since both the HOMO and the LOMO levels are in general stabilized with branching, it would be intuitively quite acceptable if the total π -electron energy—which is in fact a measure of the mean value of occupied orbital energies²⁸—would also be shifted in the same direction. This, however, is not the case and leads to

Rule 3: Total π -electron energy (in β units) decreases with the increase of branching.

Rule 3 can be shown to be valid in all cases considered. In fact, for tree graphs with $K=1$ the equation

$$E_r = E_r(L_N) - 0.09 T \quad (50)$$

is fulfilled to a high degree of accuracy, the value of the

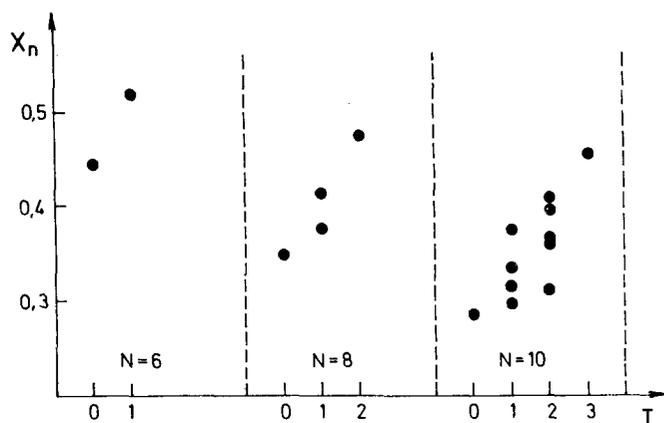


FIG. 3. The change of the HOMO level with branching.

energy decrease per branch ($0.09 \approx 0.1 \beta$) is the mean value for all branched molecular trees with $N=6, 8$, and 10 vertices. In passing we also note that in the parameterization scheme recently proposed by Hess and Schaad,²⁹ the decrease of E_r with branching is included implicitly.

The behavior of E_r , x_1 , and x_n implies that branching must cause peculiar rearrangements and not only simple shifts in the MO energy level distribution pattern, and that the density of distribution of the eigenvalues in the graph spectrum becomes highly nonuniform. This will be a matter of further investigation.

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³We call "molecular topology" the totality of information contained in the molecular graph.⁴ If a physical or chemical property of a molecule is largely determined by molecular topology, it is called a "topological property."

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