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A Graph-Theoretical Study of Conjugated Systems Containing a Linear Polyene Fragment

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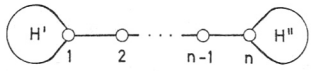
Conjugated molecules containing a linear polyene fragment are studied using graph theory. It is shown that the characteristic polynomials of the molecular graphs of these systems fulfill a common recurrence relation and have, therefore, a common general form. The spectra of 10 classes of such graphs are obtained in analytical form. These spectra are mutually related and are also related to the spectrum of cycles (which are molecular graphs of annulenes). From the spectra obtained analytical expressions for total π-electron energy, HOMO-LUMO separation, *etc.* are deduced.

INTRODUCTION

In the present paper conjugated systems of the general form



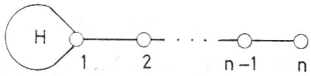
G_n

will be studied. Graph theoretical terminology will be used[1,2], but it should be noted that this is only another form of expressing Hückel molecular orbital results.

Hückel theory of linear polyenes and their different derivatives is a topic with a long history[3] and is described in detail in textbooks of quantum chemistry[4]. Nevertheless, there have also been various recent investigations in this field[5–7], showing that all aspects of the problem are still not solved.

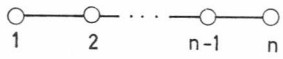
The graph G_n can be defined in the following manner. It is connected and contains a sequence of vertices j ($j = 2, 3, \ldots, n-1$) which are all of degree two and the vertex j is joined to the vertices $j-1$ and $j+1$. If the edge between the vertices j and $j+1$ is deleted from G_n, the resulting graph will have two components. These components are the graphs H'_j and H''_{n-j} (see discussion later). The class of all graphs with such properties will be denoted by $\mathbf{L}_n$. The characteristic polynomial[2] of the graph G_n will be denoted by $G_n = G_n(x)$. The spectrum of a graph is the set of roots of its characteristic polynomial. The spectrum of G_n will be denoted by $S(G_n)$.

Further, let H_n be the graph



H_n

where H is an arbitrary graph. The subgraphs H' and H'' in G_n are also arbitrary graphs. Of course, $H_n \in \mathbf{L}_n$. A special case of the graphs G_n and H_n is the chain L_n.



L_n

For the considerations which follow it is necessary to remember that the first two characteristic polynomials of L_n are defined to be

$$L_0 = 1, \quad L_1 = x \tag{1}$$

A RECURRENCE RELATION FOR G_n

It is well known[4] that the characteristic polynomial of H_n fulfills the recurrence relation

$$H_n = x\, H_{n-1} - H_{n-2} \tag{2}$$

which is a special case of a theorem of Heilbronner[8]:

$$G_n = H'_j \; H''_{n-j} - H'_{j-1} \; H''_{n-j-1} \tag{3}$$

Actually, if $G_n = H_n$, it will be $H'_k = H_k$ and $H''_k = L_k$. Now eq. (2) follows from eq. (3) for $j = n - 1$.

However, the validity of the relation (2) is more general; in particular it holds for the whole class $\mathbf{L}_n$. In order to see this, combine eqs. (3) and (2),

$$G_n = H'_j \; (x\, H''_{n-j-1} - H''_{n-j-2}) - H'_{j-1} \; (x\, H''_{n-j-2} - H''_{n-j-3}) =$$

$$= x\,(H'_j \; H''_{n-j-1} - H'_{j-1} \; H''_{n-j-2}) - (H_j \; H''_{n-j-2} - H'_{j-1} \; H''_{n-j-3})$$

which finally gives

$$G_n = x\, G_{n-1} - G_{n-2} \tag{4}$$

Therefore, eq. (4) can be understood as an algebraic characteristic of the class $\mathbf{L}_n$.

From the relation (4) it follows[9] that

$$G_n = A\,(\lambda_1)^n + B\,(\lambda_2)^n$$

where λ_1 and λ_2 are the solutions of the equation $\lambda^2 = x\,\lambda - 1$, and A and B are some functions of x. Therefore,

$$G_n = A \left(\frac{x + \sqrt{x^2 - 4}}{2} \right)^n + B \left(\frac{x - \sqrt{x^2 - 4}}{2} \right)^n$$

and if one introduces $x = 2 \cos t$,

$$G_n = A \exp (\mathrm{int}) + B \exp (-\mathrm{int})$$

where the Euler formula $\cos x \pm i \sin x = \exp (\pm i\, x)$ has been used. Another form of this relation is

$$G_n = (A + B) \cos nt + i\,(A - B) \sin nt$$

The functions A and B can be easily determined from the knowledge of, say, G_0 and G_1. Thus,

$$G_n = G_0 \cos nt + \frac{G_1 - G_0 \cos t}{\sin t} \sin nt$$

which after simple transformations becomes

$$G_n = G_1 \frac{\sin nt}{\sin t} - G_0 \frac{\sin (n-1)t}{\sin t} \tag{5}$$

This is the general form of the characteristic polynomial of a graph from the class $\mathbf{L}_n$.

Let us now consider a special case — the chain L_n. Because of eqs. (1),

$$L_n = 2 \cos t \frac{\sin nt}{\sin t} - \frac{\sin (n-1)t}{\sin t}$$

which simply gives

$$L_n = \frac{\sin (n+1)t}{\sin t} \tag{6}$$

From eq. (6) the spectrum of the chain is evident. Namely from $L_n = 0$ it follows that $(n+1)t = j\pi$ $(j = 1, 2, \ldots, n)$ and therefore,

$$S(L_n) = \left\{ 2 \cos \frac{j\pi}{n+1} \;\middle|\; j = 1, 2, \ldots, n \right\} \tag{7}$$

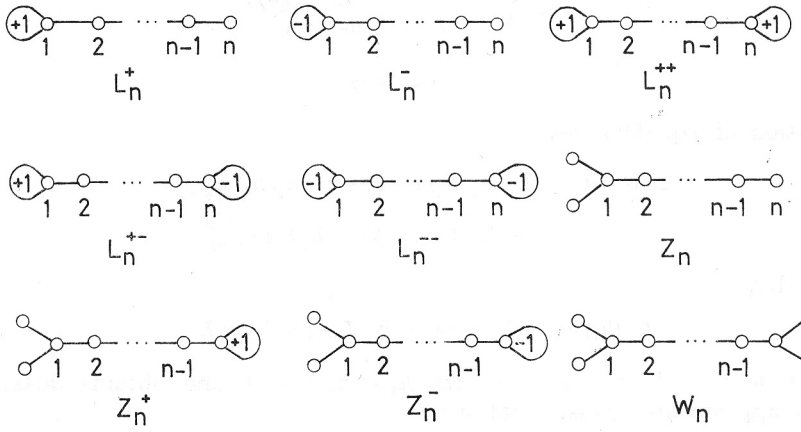
The results (6) and (7) are, of course, well known[3,4]. By substituting eq. (6) back into (5), one obtaines an additional formula for G_n

$$G_n = G_1 L_{n-1} - G_0 L_{n-2} \tag{8}$$

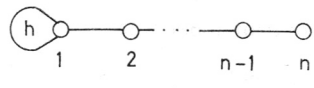
from which one can see how closely is the characteristic polynomial of a graph from $\mathbf{L}_n$ related to L_n. Note that the polynomial G_0 is, by definition, equal to $x G_1 - G_2$.

THE SPECTRA OF NINE GRAPHS FROM THE CLASS $\mathbf{L}_n$

In this section we shall derive analytical formulae for the spectra of the following graphs.



Let first consider a graph L_n^h



L_n^h

which possesses a loop of weight h on the vertex 1. This is the graph representation[10] of a heteroconjugated analogue of a linear polyene with the heteroatom in the position 1. According to eq. (8),

$$L_n^h = L_n - h\,L_{n-1} \tag{9}$$

Using eq. (6), one obtains for $h = 1$ and $h = -1$

$$L_n^+ = \frac{\cos\dfrac{(2n+1)\,t}{2}}{\cos\, t/2}$$

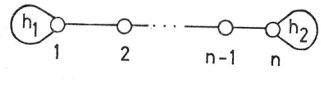
$$L_n^- = \frac{\sin\dfrac{(2n+1)\,t}{2}}{\sin\, t/2}$$

from which it follows straightforwardly that

$$S(L_n^+) = \left\{ 2\,\cos\frac{(2j+1)\,\pi}{2n+1} \;\middle|\; j = 0, 1, \ldots, n-1 \right\} \tag{10}$$

$$S(L_n^-) = \left\{ 2\,\cos\frac{2j\,\pi}{2n+1} \;\middle|\; j = 1, 2, \ldots, n \right\} \tag{11}$$

The spectra of L_n^{++}, L_n^{+-} and L_n^{--} can be obtained by considering the graph $L_n(h_1, h_2)$.



$L_n(h_1, h_2)$

Application of eq. (8) gives

$$L_n(h_1, h_2) = L_1(h_1, h_2)\,L_{n-1} - L_0(h_1, h_2)\,L_{n-2} =$$

$$(x - h_1 - h_2)\,L_{n-1} - (1 - h_1\,h_2)\,L_{n-2}$$

and finally,

$$L_n(h_1, h_2) = L_n - (h_1 + h_2)\,L_{n-1} + h_1\,h_2\,L_{n-2} \tag{12}$$

For $h_1 = h_2 = 1$, $h_1 = -h_2 = 1$ and $h_1 = h_2 = -1$ one obtains, after performing appropriate transformations,

$$L_n^{++} = 2(\cos t - 1)\frac{\sin nt}{\sin t}$$

$$L_n^{+-} = 2\cos nt \tag{13}$$

$$L_n^{--} = 2(\cos t + 1)\frac{\sin nt}{\sin t}$$

The spectra of these three graphs can be now deduced without difficulty. The relations between the spectra of L_n^{++}, L_n^{--} and L_{n-1} are evident.

$$S(L_n^{++}) = S(L_{n-1}) \cup \{2\} \tag{14}$$

$$S(L_n^{+-}) = \left\{ 2\cos\frac{(2j+1)\pi}{2n} \;\middle|\; j = 0, 1, \ldots, n-1 \right\} \tag{15}$$

$$S(L_n^{--}) = S(L_{n-1}) \cup \{-2\} \tag{16}$$

By inspection of eqs. (9) and (12) it can be concluded that analytical expressions for the characteristic polynomials and spectra can be obtained only when the parameters h have the value $+1$, 0 or -1. This seems not to be a fortuitous fact, as will be pointed out in the later discussion.

The spectra of Z_n and W_n have been obtained previously.[11,12] We list them because of completeness.

$$Z_n = 4\cos t \cos(n+1)t$$

$$S(Z_n) = \left\{ 2\cos\frac{(2j+1)\pi}{2n+2} \;\middle|\; j = 0, 1, \ldots, n \right\} \cup \{0\} \tag{17}$$

$$W_n = 16\cos^2 t\,(\cos^2 t - 1)\frac{\sin(n+1)t}{\sin t}$$

$$S(W_n) = S(L_n) \cup \{-2, 0, 0, 2\} \tag{18}$$

It is easily seen that a relation similar to (18) exists also for $S(Z_n)$:

$$S(Z_{n-1}) = S(L_n^{+-}) \cup \{0\}$$

The characteristic polynomials and spectra of the graphs Z_n^+ and Z_n^- can be deduced in an analogous manner.

$$Z_n^+ = -8\cos t \sin t/2 \sin\frac{(2n+1)t}{2}$$

$$S(Z_n^+) = \left\{ 2\cos\frac{2j\pi}{2n+1} \;\middle|\; j = 0, 1, \ldots, n \right\} \cup \{0\} \tag{19}$$

$$Z_n^- = 8\cos t \cos t/2 \cos\frac{(2n+1)t}{2}$$

$$S(Z_n^-) = \left\{ 2\cos\frac{(2j+1)\pi}{2n+1} \;\middle|\; j = 0, 1, \ldots, n \right\} \cup \{0\} \tag{20}$$

The following relations between the spectra of Z_n^+ , Z_n^- , L_n^+ and L_n^- hold.

$$S(Z_n^+) = S(L_n^-) \cup \{0, 2\}$$

$$S(Z_n^-) = S(L_n^+) \cup \{-2, 0\}$$

There are also many other relations between the spectra (7), (10), (11), (14)—(20), as well as between these spectra and the spectrum of cycles (see later).

Efforts have been made to obtain analytical expressions for spectra of other graphs from the class $\mathbf{L}_n$, but without success. That this is not a temporary failure indicates the fact that the above considered graphs are the only members of the class $\mathbf{L}_n$, the spectra of which lie in the interval $[-2, +2]$[13]. Therefore, the eigenvalues of other graphs from $\mathbf{L}_n$ cannot be presented in the form $2\cos\frac{p\pi}{q}$ (p, q integers, $q \neq 0$), and the graph-theoretical technique just outlined cannot in principle be applied for the derivation of their spectra. This justifies the formulation of the following conjecture.

Conjecture

Graphs L_n , L_n^+ , L_n^- , L_n^{++} , L_n^{+-} , L_n^{--} , Z_n , Z_n^+ , Z_n^- and W_n are the only ten graphs from the class $\mathbf{L}_n$, the spectra of which can be expressed in analytical form.

SOME QUANTUM CHEMICAL CHARACTERISTICS OF THE GRAPHS L_n^h AND $L_n(h_1, h_2)$

An inspection of the spectra of the ten graphs which were considered in the previous section shows that there are no degenerate energy levels in the corresponding molecules, except the degenerate non-bonding levels in Z_n and W_n (see Table). Because of the convenient form of the spectra, analytical expressions for total π-electron energy, E_π, and HOMO-LUMO separation* can be easily calculated. These expressions are presented in the Table, together with the number N_0 of non-bonding MO's and the difference between the number N_+ of bonding and the number N_- of antibonding MO's. Cycles are also included in the Table (see later). The formulae for the total π-electron energy of L_n are long known[3,14], while those of Z_n have been also published recently[11]. Note that in ref. 14 a simple but elegant method is described enabling the derivation of all analytical expressions for E_π.

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* HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital

TABLE

molecular graph	n	E_π	HOMO-LUMO separation	N_0	$N_+ - N_-$
L_n	even	$2\ \mathrm{cosec}\ \frac{\pi}{2n+2} - 2$	$4 \sin \frac{\pi}{2n+2}$	0	0
	odd	$2\ \mathrm{cotg}\ \frac{\pi}{2n+2} - 2$	$2 \sin \frac{\pi}{n+1}$	1	0
L_n^+	even	$\mathrm{cosec}\ \frac{\pi}{4n+2}$	$4 \sin \frac{\pi}{2n+1} \cos \frac{\pi}{4n+2}$	0	0
	odd	$\mathrm{cosec}\ \frac{\pi}{4n+2} \cos \frac{\pi}{2n+1}$	$4 \sin \frac{\pi}{2n+1} \cos \frac{\pi}{4n+2}$	0	1
L_n^-	even	$\mathrm{cosec}\ \frac{\pi}{4n+2} - 2$	$4 \sin \frac{\pi}{2n+1} \cos \frac{\pi}{4n+2}$	0	0
	odd	$\mathrm{cosec}\ \frac{\pi}{4n+2} \cos \frac{\pi}{2n+1} - 2$	$4 \sin \frac{\pi}{2n+1} \cos \frac{3\pi}{4n+2}$	0	-1
L_n^{++}	even	$2\ \mathrm{cotg}\ \frac{\pi}{2n} + 2$	$2 \sin \frac{\pi}{n}$	1	1
	odd	$2\ \mathrm{cotg}\ \frac{\pi}{2n} \cos \frac{\pi}{2n} + 2$	$4 \sin \frac{\pi}{2n}$	0	1
L_n^{+-}	even	$2\ \mathrm{cosec}\ \frac{\pi}{2n}$	$4 \sin \frac{\pi}{2n}$	0	0
	odd	$2\ \mathrm{cotg}\ \frac{\pi}{2n}$	$2 \sin \frac{\pi}{n}$	1	0
L_n^{--}	even	$2\ \mathrm{cotg}\ \frac{\pi}{2n} - 2$	$2 \sin \frac{\pi}{n}$	1	-1
	odd	$2\ \mathrm{cotg}\ \frac{\pi}{2n} \cos \frac{\pi}{2n} - 2$	$4 \sin \frac{\pi}{2n} \cos \frac{\pi}{n}$	0	-1
Z_n	even	$2\ \mathrm{cotg}\ \frac{\pi}{2n+2}$	0	2	0
	odd	$2\ \mathrm{cosec}\ \frac{\pi}{2n+2}$	$2 \sin \frac{\pi}{2n+2}$	1	0

molecular graph	n	E_π	HOMO-LUMO separation	N_0	$N_+ - N_-$
Z_n^+	even	$\operatorname{cosec} \frac{\pi}{4n+2} + 2$	$2 \sin \frac{\pi}{4n+2}$	1	1
	odd	$\operatorname{cosec} \frac{\pi}{4n+2} + 2$	$2 \sin \frac{3\pi}{4n+2}$	1	0
Z_n^-	even	$\operatorname{cosec} \frac{\pi}{4n+2}$	$2 \sin \frac{\pi}{4n+2}$	1	−1
	odd	$\operatorname{cosec} \frac{\pi}{4n+2}$	$2 \sin \frac{3\pi}{4n+2}$	1	0
W_n	even	$2 \operatorname{cosec} \frac{\pi}{2n+2} + 2$	0	2	0
	odd	$2 \operatorname{cotg} \frac{\pi}{2n+2} + 2$	0	3	0
C_n	$4m$	$4 \operatorname{cotg} \frac{\pi}{n}$	0	2	0
	$4m+1$	$2 \operatorname{cotg} \frac{\pi}{2n} \cos \frac{\pi}{2n}$	$4 \sin \frac{\pi}{n} \cos \frac{\pi}{2n}$	0	1
	$4m+2$	$4 \operatorname{cosec} \frac{\pi}{n}$	$4 \sin \frac{\pi}{n}$	0	0
	$4m+3$	$2 \operatorname{cotg} \frac{\pi}{2n} \cos \frac{\pi}{2n}$	0	0	−1

For large values of n,

$$\operatorname{cosec} \frac{\pi}{a\,n+b} \approx \operatorname{cotg} \frac{\pi}{a\,n+b} \approx \frac{a\,n+b}{\pi}$$

and

$$\cos \frac{\pi}{an+b} \approx 1$$

which essentially simplifies the form of the expression for E_π. Hence, for a sufficiently long polyene chain,

$$E_\pi = \frac{4}{\pi} n + T \qquad (21)$$

with

$$T = \begin{cases} \frac{4}{\pi} - 2 + (2 - \frac{2}{\pi})\, n^+ - \frac{2}{\pi}\, n^- & \text{for } L_n,\ L_n^+,\ L_n^-,\ L_n^{++},\ L_n^{+-} \text{ and } L_n^{--} \\ \frac{4}{\pi} + (2 - \frac{2}{\pi})\, n^+ - \frac{2}{\pi}\, n^- & \text{for } Z_n,\ Z_n^+ \text{ and } Z_n^- \\ \frac{4}{\pi} + 2 & \text{for } W_n \end{cases}$$

n^+ and n^- are the number of loops with weight $+1$ and -1, respectively, in the graph considered. This form of the function T can be proved by testing it individually for each of the ten graphs in turn.

Numerical calculations show[6,15] that the linear relation (21) is a satisfactory approximation except for the smallest values of n. Another form of eq. (21) is

$$\lim_{n \to \infty} \frac{E_\pi}{n} = \frac{4}{\pi} \tag{22}$$

According to a theorem of Stankevich[16], the relation (22) holds for every graph of the class $\mathbf{L}_n$.

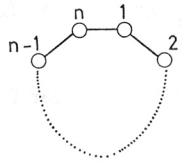
In the subsequent discussion we shall consider the influence of loops on several π-electron characteristics of the conjugated systems presented by graphs L_n^h and L_n (h_1, h_2). Note that the weight h of a loop is related to the electronegativity of the corresponding heteroatom[17,7]. As can be seen from Table, $h = 1$ in general increases, while $h = -1$ decreases, the value of $N_+ - N_-$. This means that the presence of a heteroatom indicated by a loop with weight $h > 0$ $(h < 0)$ increases (decreases) the electron affinity and decreases (increases) the ionisation potential of the molecule[18].

The magnitude of the HOMO-LUMO separation in linear polyenes is to a large extent independent of the number of loops and their weights, and is approximately equal to $2\pi/n$ (in β units), except, of course, for systems with non-bonding π-electron levels. The prediction that the HOMO-LUMO separation in the class of polyenes considered vanishes for large n is not supported by experimental findings[19,20]. However, this is also the failure of other, more sophisticated MO approaches[21], and could be overcome only within the unrestricted Hartree-Fock approximation[5].

The final point which we mention here is that, unexpectedly, E_π is unequally sensitive to the presence of loops with positive and negative weight. Eq. (21) indicates that positive loops increase the value of E_π (in β units) by nearly $2 - 2/\pi \approx 1.36$ times the total weight of these loops. However, negative loops decrease E_π by only $2/\pi \approx 0.64$ times the total weight of such loops. As a consequence of this, the graph L_n^{+-} represents a more stable molecule than a linear polyene hydrocarbon with n carbon atoms (represented by L_n). At present there is no available explanation for this interesting phenomenon.

ON THE SPECTRUM OF A CYCLE

The spectrum of a cycle, C_n, is well known. For a recent discussion on



C_n

this problem and further references see ref. (22). In order to show the relationship between the spectra of C_n and L_n, remember that according to the Sachs theorem[2], the following relation is valid for the characteristic polynomial of a graph G.

$$G(x) = \sum_{s \in \mathbf{S}} (-1)^{c(s)} \; 2^{r(s)} \; x^{N-v(s)}$$

where s is a Sachs graph with $c(s)$ components, $r(s)$ cyclic components and $v(s)$ vertices. N is the number of vertices of the graph G. $\mathbf{S}$ is the set of all Sachs graphs of G, and the summation goes over all elements of $\mathbf{S}$.

Now let us consider a subset $\mathbf{S}_a$, the elements of which are all graphs from $\mathbf{S}$ having $r(s) = 0$. This enables one to define a new polynomial

$$G^a(x) = \sum_{s \in \mathbf{S}_a} (-1)^{c(s)} \; x^{N-v(s)}$$

which we call the acyclic polynomial of the graph G and its roots form the acyclic spectrum of G. These concepts have recently been applied in the study of resonance energies of conjugated molecules[23].

It can be shown[23] that G^a fulfills a generalization of the Heilbronner relation (3), namely

$$G^a = (G-e)^a - (G-[e])^a \tag{23}$$

where $G-e$ is the graph obtained by deleting the edge e from G, and $G-[e]$ is obtained by deleting from G the edge e and its two incident vertices. The application of eq. (23) to C_n gives

$$(C_n)^a = (L_n)^a - (L_{n-2})^a$$

But L_n contains no cycles at all, and therefore $(L_n)^a = L_n$. Now it can be easily seen that

$$(C_n)^a = L_n^{+-} \tag{24}$$

and hence the acyclic polynomial and acyclic spectrum of C_n are identical with the characteristic polynomial and spectrum of the graph L_n^{+-} studied earlier.

Finally, let us deduce the spectrum of C_n. Since C_n possesses exactly one cyclic Sachs graph (with $c(s) = 1$, $r(s) = 1$, $v(s) = n$),

$$C_n = (C_n)^a - 2$$

which together with eqs. (13) and (24) gives the well known formulae

$$C_n = 2 \cos nt - 2$$

$$S(C_n) = \left\{ 2 \cos \frac{2j\pi}{n} \;\middle|\; j = 1, 2, \ldots, n \right\}$$

For reasons of completeness, analytical expressions for E_π and the HOMO--LUMO separation of cycles are also presented in the Table.

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SAŽETAK

Studij konjugiranih sustava koji sadrže kao fragment linearni polien pomoću teorije grafova

Ivan Gutman

Konjugirane molekule koje kao fragment sadrže linearni polien studirane su pomoću teorije grafova. Pokazano je da karakteristični polinomi molekularnog grafa ovih sustava zadovoljavaju jednu zajedničku rekurentnu relaciju, te prema tome imaju isti opći oblik. Dobiveni su analitički izrazi za spektre 10 klasa ovakvih grafova. Ovi spektri su povezani kako međusobno tako i sa spektrima kontura (koje su molekularni grafovi anulena). Iz dobivenih spektara izvedeni su analitički izrazi za ukupnu π-elektronsku energiju, HOMO-LUMO cijepanje itd.

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