On Relative Stabilities of Distinct Polyenes. An Extension of the Concept of Conjugated Paths

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Abstract

The study continues the previous development [MATCH, 72 (2014) 39-73] of the perturbative approach to relative stabilities of pi-electron systems of conjugated hydrocarbons modeled as sets of weakly-interacting initially-double (C=C) bonds. Distinct isomers of acyclic hydrocarbons (polyenes) are now under focus. The relevant total pi-electron energies ($E$) are expressed in the form of power series containing members ($E_{(k)}$) of even orders ($k = 0, 2, 4, ...$) with respect to the averaged resonance parameter of initially-single (C-C) bonds. Terms to within the sixth order ($k = 6$) inclusive are shown to be of importance for discrimination between similar isomers. In this connection, missing expressions for corrections $E_{(6)}$ are originally derived. Conjugated paths of various lengths (i.e. linear chains consisting of C=C and C-C bonds alternately) are shown to be the most important (but not the only) fragments contributing to stabilization of any acyclic pi-electron system. Again, new types of fragments (substructures) are revealed (viz. the so-called composite conjugated paths) that contribute to destabilization of the system concerned. As a result, formation of the total energy of an acyclic pi-electron system is concluded to be governed by an interplay between stabilizing and destabilizing factors. Accordingly, the perturbative approach applied offers us an extension of the concept of conjugated paths. Particular isomers containing four, five and six C=C bonds are considered in a detail as examples.

1 Introduction

Qualitative intuition-based concepts and models play a crucial role in chemistry throughout its history. Accordingly, attempts to derive them deductively from more
sophisticated quantum-chemical approaches contribute to our understanding of the nature of the given concept and/or model, as well as indicate directions for its possible extensions and improvements.

The concepts of conjugated paths [1] and circuits [2-4] are successfully applied to evaluate relative stabilities of pi-electron systems of similar conjugated hydrocarbons [5], e.g. of various isomers of polyenes and of different Kekulé valence structures of a certain benzenoid, respectively. Chains and cycles consisting of double (C=C) and single (C-C) bonds alternately are regarded here as the principal substructures determining stabilities of the structures concerned. Some limitations of these concepts also have been reported [5-8]. Difficulties in discriminating between stabilities of isomers of extended polyenes characterized by slightly different types of branching [5] are especially noteworthy in the context of the present study.

In general, interpretation of stability of a certain pi-electron system depends on the model applied. Given that the latter coincides with the molecular graph [5, 9-11], the vertices and edges of which represent carbon atoms and carbon-carbon bonds, respectively, the relevant total energy is discussed in terms of properties of this graph (see e.g. [12,13]). Another alternative consists in modeling of a conjugated system as a set of weakly-interacting initially-double (C=C) bonds and thereby in employment of the perturbation theory to evaluate and to rationalize relative stabilities of isomers. Although the second option traditionally refers to acyclic conjugated hydrocarbons [14], adequacy of perturbative approaches to individual Kekulé valence structures of benzenoids also is beyond any doubt [15]. Again, an evident analogy between the perturbational perspective to pi-electron systems and that underlying the concepts of conjugated paths and circuits gives us a hint about feasibility of a perturbation-theory-based derivation of these concepts followed by their extensions (if necessary).

The above-formulated task, however, is not easily achievable. Difficulties in application to extended conjugated hydrocarbons of the most popular perturbational molecular orbital (PMO) theory [14] may be mentioned among the principal reasons here. Indeed, the original Dewar formula for the second order energy ($E_{(2)}$) underlying this theory yields coinciding stabilities of numerous important pi-electron systems of distinct constitutions, including different Kekulé valence structures of benzenoids and
isomers of polyenes. To circumvent this difficulty, reference structures of artificial and involved nature are invoked instead of sets of C=C bonds, e.g. two allyle radicals for a Kekulé valence structure of benzene [14]. Such an option, however, makes the overall approach even more remote from the concepts of conjugated paths and circuits.

An alternative to the standard PMO theory has been suggested recently [15,16], wherein corrections of higher orders (\(E_3\), \(E_4\), etc.) of the power series for total energies (\(E\)) have been taken into consideration along with second order ones (\(E_2\)) instead of passing to the above-discussed artificial reference structures. Thus, the classical model of conjugated hydrocarbons as sets of weakly-interacting C=C bonds has been preserved in this new approach. At the same time, the latter exhibited a much higher discriminative potential as compared to that of the standard PMO theory (which was shown to depend upon the number of corrections actually included). Besides, compact and chemically illustrative expressions for corrections \(E_3\), \(E_4\) [15-17] and \(E_5\) [15] have been derived using an original matrix form of the perturbation theory (PT), namely the so-called non-commutative Rayleigh-Schrödinger perturbation theory (NCRSPT) [18-20]. Application of the latter approach to individual Kekulé valence structures of benzenoid hydrocarbons has been carried out in the recent study [15]. Contributions both of linear (acyclic) and of cyclic conjugated fragments (substructures) were shown to be taken into consideration on the unified basis in the power series for total energies. This implies the approach employed to embrace perturbative analogues of both conjugated paths and circuits formally present in the structures concerned. The above-mentioned contributions, however, are not easily separable one from another. That is why no attempts were made to extend the qualitative concepts either of conjugated paths or of circuits in this study.

The present article addresses a more simple case of acyclic conjugated hydrocarbons (polyenes) containing no conjugated circuits. Our aim now consists in a deductive revealing the principal types of conjugated fragments (substructures) contributing to the relevant total pi-electron energies and thereby in justifying and/or extending the concept of conjugated paths. At the same time, the extension being sought might be relevant also to numerous related concepts, such as conjugated paths invariants [21], the mean length of conjugated paths [22], conjugation paths used in
studies of donor/acceptor functionalized pi-electron systems [23,24], etc. To achieve
the above-formulated end, the same perturbative approach will be applied along with
the experience of Ref.[15]. In respect of the latter, the following points deserve men-
tioning: First, energy corrections of odd orders proved to take non-zero values for
conjugated- circuits- containing systems only. Thus, we may now confine ourselves to
members of the power series of even orders only. Second, energy increments $E_{(0)}$ and
$E_{(2)}$ were shown to be determined by total numbers of C=C and C-C bonds of the
given structure, respectively. Thus, these corrections are expected to take coinciding
values for isomers of the same hydrocarbon. In this connection, corrections at least
of fourth and sixth orders seem to be required to discriminate between stabilities of
these isomers. Thus, formulae for sixth order energies are originally derived in the
Appendix of the present study.

The paper starts with a brief overview of the principal expressions of the approach
to be applied (Sect. 2). Thereupon, we turn to revealing the principal types of
conjugated fragments that contribute to the energy corrections $E_{(4)}$ and $E_{(6)}$ (Sect.
3). The final section is devoted to relative stabilities of specific polyenes.

2 Expressions for energy corrections

As already mentioned, acyclic conjugated hydrocarbons (polyenes) will be considered
as sets of weakly-interacting initially-double (C=C) bonds. Moreover, the systems
concerned belong to even alternant hydrocarbons (AHs) [9-11, 25,26]. The above-
mentioned two points will be taken into consideration when constructing the relevant
Hückel type Hamiltonian matrix ($H$).

Let the pi-electron system of a certain polyene to be initially represented by an
$2N-$dimensional basis set of $2p_z$ AOs of carbon atoms $\{\chi\}$, where $N$ stands for the
total number of C=C bonds. These AOs will be assumed to be characterized by
uniform Coulomb parameters ($\alpha$) as usual and the equality $\alpha = 0$ will be accepted.
As with the standard Hückel model (see e.g. [9,25]), resonance parameters between
AOs of chemically bound pairs of atoms only will be assumed to take non-zero values.
Further, let the basis set $\{\chi\}$ to be divided into two $N$-dimensional subsets $\{\chi^*\}$ and
so that pairs of orbitals belonging to any chemical bond (C=C or C-C) find themselves in the different subsets. This implies the non-zero resonance parameters to take place in the off-diagonal (inter-subset) blocks of the Hamiltonian matrix \( \mathbf{H} \). Accordingly, zero submatrices stand in the diagonal (intra-subset) positions of the matrix \( \mathbf{H} \) as it is peculiar to AHs in general [9, 25, 26]. Finally, let us enumerate the basis functions in such a way that orbitals belonging to the same C=C bond acquire the coupled numbers \( i \) and \( N + i \). As a result, resonance parameters of these strong bonds take the diagonal positions in the intersubset blocks of the matrix \( \mathbf{H} \). Uniform values of these parameters (\( \beta \)) also is among natural assumptions here. Let our (negative) energy unit to coincide with \( \beta \) in addition. The usual equality \( \beta = 1 \) then immediately follows. Similarly, the averaged resonance parameter of weak (C-C) bonds will be denoted by \( \gamma \) and supposed to be a first order term vs. the above-specified energy unit.

In summary, Hamiltonian matrices of pi-electron systems of polyenes (\( \mathbf{H} \)) take a common form that may be represented as a sum of zero (\( \mathbf{H}(0) \)) and first order matrices (\( \mathbf{H}(1) \)) including parameters of C=C and C-C bonds, respectively, viz.

\[
\mathbf{H} = \mathbf{H}(0) + \mathbf{H}(1) = \begin{bmatrix} 0 & \mathbf{I} & 0 \\ \mathbf{I} & 0 & 0 \\ 0 & \gamma \mathbf{B}^+ & 0 \end{bmatrix}, \tag{1}
\]

where \( \mathbf{I} \) here and below stands for the unit matrix and the superscript + designates the transposed (Hermitian-conjugate) matrix. It deserves adding here that unit off-diagonal elements of the submatrix \( \mathbf{B} \) (\( B_{ij} = 1, i \neq j \)) correspond to C-C bonds, otherwise these take zero values. Meanwhile, the diagonal elements of the same submatrix (\( B_{ii} \)) vanish because entire resonance parameters of C=C bonds are included into the zero order matrix \( \mathbf{H}(0) \).

The Hamiltonian matrix of Eq. (1) coincides with that representing Kekulé valence structures of benzenoids [15] because of similar constitutions of both systems. Accordingly, the subsequent steps towards derivation of the relevant energy corrections also are similar. Thus, we start with passing to a new basis \( \{ \varphi \} \) consisting of bonding and antibonding orbitals of C=C bonds defined as normalized sums and differences of pairs of AOs \( \chi_i^* \) and \( \chi_{N+i}^0 \) and referred to below as bond orbitals. The transformed Hamiltonian matrix then meets the requirements of the NCRSPT (see the Appendix).
As a result, general formulae for members of the power series for total energies ($E$) may be applied that have been derived earlier [15-17] using this PT [18-20]. As already mentioned (Sect.1), we confine ourselves to terms $E(k)$ of even orders ($k = 0, 2, 4, ..$). Let us turn now to individual members of the power series.

The zero order energy ($E(0)$) coincides with $2N$, whatever the specific structure of the given system. The subsequent second order member ($E(2)$) takes a rather simple form, viz.

$$E(2) = 4 Tr(G(1)G^+_1) > 0,$$

whereas the fourth order one ($E(4)$) consists of a sum of two components [16]:

$$E^{(+)\, (4)} = 4 Tr(G(2)G^+_2) > 0, \quad E^{(-)\, (4)} = -4 Tr(G(1)G^+_1 G(1)G^+_1) < 0.$$

The notation $Tr$ here and below stands for a Trace of the whole matrix product within parentheses, and $G(1)$ and $G(2)$ are the principal matrices of the NCRSPT [17-20] of the first and second orders, respectively, specified below. As is seen from Eqs. (2) and (3), Traces of positive-definite matrices [27] of the type $AA^+$ stand in these relations. Thus, sums of squares of elements of matrices $G(1)$, $G(2)$ and $G(1)G^+_1$ are contained there. This implies an a priori positive sign of the second order energy $E(2)$. Meanwhile, the components of the fourth order correction $E(4)$ are of opposite signs as indicated by additional superscripts $(+)$ and $(-)$.

Let us now dwell on matrices $G(1)$ and $G(2)$ [17-20]. In the particular case of the NCRSPT employed in the present study (see the Appendix), these matrices are expressible as follows

$$G(1) = -\frac{1}{2}R, \quad G(2) = -\frac{1}{2} (SG(1) - G(1)Q) = \frac{1}{4} (SR - RQ) = \frac{1}{4} (SR + RS),$$

where matrices $S$, $Q$ and $R$ contain resonance parameters between the above-specified bond orbitals (BOs) $\{\varphi\}$. Let bonding BOs (BBOs) and the antibonding ones (ABOs) to be correspondingly denoted by subscripts $(+)$ and $(-)$, e.g. $\varphi_{(+i)}$ and $\varphi_{(-l)}$ will stand for the BBO of the Ith C=C bond and for the ABO of the Lth one, respectively. Individual elements of matrices $S$, $Q$ and $R$ may be then explicitly expressed as follows

$$S_{ij} = <\varphi_{(+i)} | \hat{H} | \varphi_{(+j)} >, \quad Q_{lm} = <\varphi_{(-l)} | \hat{H} | \varphi_{(-m)} >, \quad R_{il} = <\varphi_{(+i)} | \hat{H} | \varphi_{(-l)} >.$$

(5)
where the BOs concerned are shown inside the bra- and ket-vectors. At the same time, the new matrices $S$, $Q$ and $R$ are related to the principal submatrices ($\gamma B$ and $\gamma B^+$) of our initial Hamiltonian of Eq.(1), viz.

$$S = -Q = \frac{\gamma}{2}(B + B^+), \quad R = \frac{\gamma}{2}(B^+ - B). \quad (6)$$

It is seen that matrices $S(Q)$ and $R$ are proportional to the symmetric (Hermitian) and skew-symmetric (skew-Hermitian) parts of the matrix $B$, respectively. On this basis, $G(1)$ and $G(2)$ of Eq.(4) may be easily shown to be skew-symmetric (skew-Hermitian) matrices [28]. After an additional invoking the above-mentioned equality $B_{ii} = 0$ for any $i$, we then obtain that

$$S_{ii} = Q_{ii} = R_{ii} = G(1)_{ii} = G(2)_{ii} = 0, \quad (7)$$

i.e. matrices embraced by Eq.(7) contain zero diagonal elements. A formal coincidence between matrices $S$ and $-Q$ also is seen from Eq.(6). Just this circumstance allows us to eliminate the matric $Q$ as shown in the last relation of Eq.(4). It deserves adding finally that the matrix product $G(1)G^+(1)$ determining the negative component of the fourth order energy ($\mathcal{E}_{(4)}^(-)$) is a symmetric (Hermitian) matrix. Consequently, diagonal elements $(G(1)G^+(1))_{ii}$ take non-zero values and prove to be responsible for a large part of this energy component [16].

The energy correction of the sixth order ($\mathcal{E}_{(6)}$) is derived in the Appendix. Four components reveal themselves in this correction, viz.

$$\mathcal{E}_{(6)}^{(+)} = 4Tr(G(3)^o G(3)^{o+}) > 0, \quad (8)$$

$$\mathcal{E}_{(6)}^{(-)} = 8Tr(G(1)G(1)^+ G(1)G(1)^+ G(1)G(1)^+) > 0, \quad (9)$$

$$\mathcal{E}_{(6)}^{(-)} = -32Tr[(G(1)G(2)^+ G(1)G(2)^+ G(2))] \equiv -32Tr[(G(1)G(2)^+ G(2))] < 0, \quad (10)$$

$$\mathcal{E}_{(6)}^{(u)} = 8Tr(G(1)G(2)^+ G(1)G(2)^+ G(2)^+) \equiv 8Tr[(G(1)G(2)^+ G(2))] > 0, \quad (11)$$

where

$$G(3)^o = -\frac{1}{2}(SG(2) - G(2)Q) = -\frac{1}{8}[(S)^2R + 2SRS + R(S)^2]. \quad (12)$$

The superscript $o$ is used here to distinguish the above-introduced matrix $G(3)^o$ from the standard third order matrix of the NCRSPT $G(3)$ defined by Eqs. (A5) and (A6).
The components of Eqs.(8) and (9) resemble $E^{(+)}_{(4)}$ of Eq.(3) in respect of both an *a priori* positive sign and skew-symmetric (skew-Hermitian) nature of underlying matrices $G_{(3)}^o$ and $G_{(1)}G_{(1)}^+G_{(1)}$, respectively. These components are correspondingly designated by additional subscripts 1 and 2. Accordingly, the only *a priori* negative component is shown in Eq.(10). The latter is alternatively expressible in terms of matrix products either $G_{(1)}G_{(2)}^+$ or $G_{(1)}^+G_{(2)}$. Meanwhile, the sign of the last component of the sixth order energy of Eq.(11) cannot be established *a priori* and the superscript ($u$) (undefined) is used.

Let us dwell now on interpretation of elements of the principal matrices determining our energy increments of Eqs.(2) and (3) and (8)-(11). Let us start with the simplest matrices $G_{(1)}$, $G_{(2)}$ and $G_{(3)}^o$. As is seen from Eqs.(4) and (5), the element $G_{(1)il}$ connects the BBO $\varphi_{(+i)}$ and the ABO $\varphi_{(-l)}$. Moreover, it is proportional to the relevant resonance parameter ($R_{il}$) and inversely proportional to the energy gap between BBOs and ABOs (equal to 2). Consequently, this element represents the direct (through-space) interaction between BOs $\varphi_{(+i)}$ and $\varphi_{(-l)}$. Besides, direct intrabond interactions $G_{(1)ii}$ vanish (see Eq.(7)). Again, the one-to-one correspondence between non-zero elements of the matrix $B$ and C-C bonds along with Eq.(6) allows us to expect non-zero direct interactions ($G_{(1)il} \neq 0$) to refer to BOs ($\varphi_{(+i)}$ and $\varphi_{(-l)}$) belonging to first-neighbouring C=C bonds only, the latter coinciding with those connected by a C-C bond. Further, the second order elements $G_{(2)il}$ are accordingly interpretable as indirect (through-bond) interactions of the same BOs. Indeed, from Eq.(4) we obtain

$$G_{(2)il} = \frac{1}{4}[\sum_{(+j)} S_{ij} R_{jl} - \sum_{(-m)} R_{im} Q_{ml}],$$

where sums over $(+)j$ and over $(-)m$ correspondingly embrace all BBOs and all ABOs of the given system. It is seen that both BBOs ($\varphi_{(+j)}$) and ABOs ($\varphi_{(-m)}$) of other bonds play the role of mediators here [Note that $j \neq i$ and $m \neq l$ because of Eq.(7)]. Moreover, the orbitals $\varphi_{(+j)}$ and $\varphi_{(-m)}$ should overlap directly both with $\varphi_{(+i)}$ and with $\varphi_{(-l)}$ to be efficient mediators. That is why non-zero indirect interactions correspond to pairs of second-neighbouring C=C bonds possessing a common first neighbour. Analogously, the third order elements $G_{(3)il}^o$ represent the indirect
interactions of the same BOs by means of two mediators. Pairs of BOs \( (\varphi_i^+, \varphi_1) \), \( (\varphi_1, \varphi_2) \) and \( (\varphi_2, \varphi_i^-) \) should overlap directly in this case, where \( \varphi_1 \) and \( \varphi_2 \) stand for mediating orbitals.

Elements of matrix products determining the energy components \( \mathcal{E}^{(-)}_{(4)}, \mathcal{E}^{(+)}_{(6)}, \mathcal{E}^{(-)}_{(6)} \) and \( \mathcal{E}^{(u)}_{(6)} \) also may be interpreted as indirect interactions of BOs. For example, the element \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(1)} \mathbf{G}^{(1)}_l)_{il} \) represents a certain specific indirect interaction between BOs \( \varphi_{(+)i} \) and \( \varphi_{(-)l} \), wherein the mediating orbitals necessarily coincide with an ABO \( \varphi_{(-)1} \) and a BBO \( \varphi_{(+)2} \), respectively, whilst the interaction itself consists of three successive direct interactions \( G^{(1)}_{(1)i1}, G^{+}_{(1)12} \) and \( G^{(1)}_{(1)2l} \) referring to pairs of BOs \( (\varphi_{(+)i}, \varphi_{(-)1}) \), \( (\varphi_{(-)1}, \varphi_{(+)2}) \) and \( (\varphi_{(+)2}, \varphi_{(-)l}) \). Non-zero values of these direct components evidently are required to ensure a non-vanishing third order element \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(1)} \mathbf{G}^{(1)}_l)_{il} \). Similarly, an element \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(2)} ij \) involves a direct and an indirect interaction. Besides, pairs of bonding BOs play the role of interacting orbitals for elements both \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(1)} \mathbf{G}^{(1)}_l)_{ij} \) and \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(2)} ij \), e.g. the element \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(1)} ij \) represents the indirect interaction between BBOs \( \varphi_{(+)i} \) and \( \varphi_{(+)j} \) via ABOs of the first-neighbouring C=C bonds. It is evident that the mediating ABO should overlap with both \( \varphi_{(+)i} \) and \( \varphi_{(+)j} \) in this case too. Accordingly, the diagonal element \( (\mathbf{G}^{(1}_i \mathbf{G}^{+}_{(1)} ii \) may be interpreted as the indirect self-interaction of the BBO \( \varphi_{(+)i} \).

In summary, the above analysis yields the following rule: Any matrix element of the kth order connecting two BOs \( \varphi_s \) and \( \varphi_t \) and determining an energy component takes a non-zero value, if there is at least a single non-zero product of resonance parameters, i.e.

\[
< \varphi_s \mid \hat{H} \mid \varphi_1 > < \varphi_1 \mid \hat{H} \mid \varphi_2 > ... < \varphi_{k-2} \mid \hat{H} \mid \varphi_{k-1} > < \varphi_{k-1} \mid \hat{H} \mid \varphi_t > \neq 0, \quad (14)
\]

where \( \varphi_1, \varphi_2, ... \varphi_{k-1} \) stand for mediating orbitals. Given that the condition of Eq.(14) is met, we will say that in the given system there is a pathway of the (k-1)th order between BOs \( \varphi_s \) and \( \varphi_t \). In the case of diagonal elements, we will accordingly have to deal with self-returning pathways. Besides, steps inside the same C=C bond are not allowed in these pathways because of Eq.(7). It also deserves emphasizing that the term a pathway (over BOs) is used here and below to make a distinction from conjugated paths defined in terms of chemical bonds.
After returning to the power series for total energies of Eqs. (2), (3) and (8)-(11), we may finally conclude that the higher is the order parameter \( k \), the more extended fragment of the whole system generally is embraced by the given correction \( \mathcal{E}(k) \). In this respect, the present series resembles the graph-theoretic cluster expansion for total energy [29], as well as the expansion in terms of moments [30].

### 3 Conjugated fragments contributing to total energies of polyenes

As discussed already (Sect. 2) separate increments to total energies are determined by matrices \( G^{(1)}, G^{(2)}, G^{(3)}_0, G^{+}_{(1)} G^{(1)}_0 \), etc. Thus, we will look for relations between elements of these matrices, on the one hand, and conjugated fragments present in the given system, on the other hand. The above-enumerated matrices are collected below into three groups that are analyzed separately.

#### 3.1 Relations between elements of matrices \( G^{(1)} \) and \( G^{(2)} \) and the simplest conjugated paths

Let us start with elements of the first order matrix \( G^{(1)} \) defined by Eq.(4). An element \( G^{(1)}_{ij} \) (as well as \( G^{(1)}_{ji} \)) takes a non-zero value, if the \( i \)th C=C bond and the \( j \)th one (the underlying orbitals \( \varphi^+_{ij} \) and \( \varphi^-_{ji} \) belong to) are connected by a C-C bond (Sect. 2). This implies non-zero elements \( G^{(1)}_{ij} G^{(1)}_{ji} \) to correspond to butadiene-like fragments and thereby to individual simplest conjugated paths (CPs) embracing two neighbouring C=C bonds and abbreviated below as CP(2)s. Moreover, the above-specified significant elements are local in their nature and, consequently, take uniform values for all CP(2)s. Let us also recall that the matrix \( G^{(1)} \) gives birth to the positive second order energy of Eq.(2). This implies all CP(2)s of the given polyene to contribute uniform stabilizing increments to the energy \( \mathcal{E}(2) \), the latter then being proportional to the total number of these paths.

To exemplify the above simple rule, let us consider a linear polyene containing \( N \) C=C bonds and its cross-conjugated counterpart (dendralene) [31]. Carbon atoms and thereby the relevant \( 2p_z \) AOs of these extended systems are assumed to be enu-
Figure 1: Isomers of octatetraene (I-IV) containing four C=C bonds (N=4). Numberings of 2p_z AOs of carbon atoms also are shown, where AOs under numbers 1,2,3,4 and 5,6,7,8 belong to subsets \{χ^∗\} and \{χ^o\}, respectively. Any initially-double bond C_K\=C_{N+K} is supposed to acquire the number K, where K=1,2,3,4.

merated as follows

\[
C_1 = C_{N+1} - C_2 = C_{N+2} - C_3 = C_{N+3} - \cdots - C_N = C_{2N},
\]

\[
C_1 = C_{N+1} - C_2(= C_{N+2}) - C_{N+3}(= C_3) - C_4(= C_{N+4}) - \cdots,
\]

where the C=C bonds placed outside the principal chain of carbon atoms of dendralene are shown within parentheses. Numbers 1,2...N and N+1, N+2...2N refer here to subsets \{χ^∗\} and \{χ^o\}, respectively [see also Fig.1, where isomers of octatetraene I and IV serve as examples of the systems concerned for N=4].

The principal first order matrices (viz. B and G(1)) of linear polyenes were shown to take a common form valid for any N [15] [these unified representations have been denoted by B(N) and G(1)(N)]. After invoking Eqs.(1),(4) and (6), analogous matrices are easily constructable also for dendralenes. Let the latter to acquire additional superscripts \(t\). For comparison, matrices G(1)(N) and G'(1)(N) are as follows

\[
G(1)(N) = -\frac{γ}{4}
\begin{bmatrix}
0 & 1 & 0 & 0 & \cdots \\
-1 & 0 & 1 & 0 & \cdots \\
0 & -1 & 0 & 1 & \cdots \\
0 & 0 & -1 & 0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{bmatrix},
\]

\[
G'(1)(N) = -\frac{γ}{4}
\begin{bmatrix}
0 & 1 & 0 & 0 & \cdots \\
-1 & 0 & -1 & 0 & \cdots \\
0 & 0 & 1 & 0 & \cdots \\
0 & 0 & -1 & 0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{bmatrix},
\]

where a standard factor \((-γ/4\) is introduced in front of matrices concerned for convenience. It is seen that two non-zero elements \(G(1)_{il}\) and \(G(1)_{hi}\) correspond to any C-C bond in these matrices and thereby to any CP(2) of our polyenes, and these elements take uniform absolute values in addition. Moreover, matrices G(1)(N) and G'(1)(N) of Eq.(15) resemble one another except for signs of some elements. As a result, the second order energies \(E(2)(N)\) and \(E'(2)(N)\) also are uniform and proportional
to $N - 1$, viz. these coincide with $\gamma^2(N - 1)/2$. Such a result causes no surprise, as both linear and cross-conjugated polyenes contain the same numbers of C-C bonds and thereby of CP(2)s for the same $N$ value.

Let us turn now to elements of the second order matrix $G_{(2)}$ defined by Eqs. (4) and/or (13). To ensure a non-zero value of the element $G_{(2)il}$ (and of $G_{(2)li}$), the underlying BOs $\varphi_{(+)}i$ and $\varphi_{(-)}l$ should belong to second-neighboring C=C bonds (Sect. 2), i.e. the Ith C=C bond and the Lth one should possess a common first neighbour coinciding with, say, the Mth C=C bond. The mutual arrangement of the three involved C=C bonds also plays an important role here: Given that the whole fragment I-M-L is of a linear constitution (see e.g. the isomer I of Fig.1), the mediating effect of the BBO $\varphi_{(+)}m$ and that of the ABO $\varphi_{(-)}m$ are added together and, consequently, a non-zero element $G_{(2)il}(G_{(2)li})$ arises. Meanwhile, the analogous increments cancel out one another for the cross-conjugated arrangement of C=C bonds I, M and J (e.g. in the isomer IV of Fig.1), and the relevant element $G_{(2)il}(G_{(2)li})$ vanishes. In summary, two non-zero elements ($G_{(2)il}$ and $G_{(2)li}$) correspond to BOs of the terminal C=C bonds (I and L) of any linear hexatriene-like fragment I-M-L and thereby to any conjugated path embracing three C=C bonds and further abbreviated as CP(3) [The remaining elements $G_{(2)im}$ and $G_{(2)ml}$ vanish because of zero intrabond resonance parameters (see Eq.(7)]. This implies the total number of non-zero elements of a certain matrix $G_{(2)}$ to coincide with the two-fold number of CP(3)s in the system under consideration. Uniform absolute values of the above-specified elements also easily follow from the definition of Eq.(4). As is seen from Eq.(3), the matrix $G_{(2)}$ determines the positive (stabilizing) component $\mathcal{E}_{(4)}^{(+)}$ of the fourth order energy that is an additive function with respect to squares of separate elements $G_{(2)il}(G_{(2)li})$ in addition. Consequently, the component $\mathcal{E}_{(4)}^{(+)}$ consists of a sum of transferable increments of individual CP(3)s and thereby it is expected to be proportional to the total number of these paths.

The above-specified linear and cross-conjugated polyenes may be taken here again as examples. For the linear isomer, Eqs. (3), (4) and (15) yield the following common


formulae

\[
\begin{bmatrix}
0 & 0 & 2 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 \\
-2 & 0 & 0 & 0 & 2 \\
0 & -2 & 0 & 0 & 0 \\
\end{bmatrix}, \quad G_{(2)}(N) = \gamma^2 \frac{16}{16}, \quad E_{(4)}^{(+)}(N) = \frac{8\gamma^4(N - 2)}{64},
\]

where \(\gamma^4/64\) is used here and below as a "subsidiary" unit of the fourth order energy [15,16]. Elements of the matrix \(G_{(2)}(N)\) are chosen to coincide with 2 by choice of the front factor \(\gamma^2/16\) instead of \(\gamma^2/8\) [15,16] in order to reflect participation of mediating orbitals in pairs (e.g. \(\varphi_{(+)m}\) and \(\varphi_{(-)m}\)) more conveniently. The expression for \(G_{(2)}(N)\) of Eq.(16) illustrates the above-concluded one-to-one correspondence between non-zero elements of the matrix \(G_{(2)}\) and individual CP(3)s. Proportionality between \(E_{(4)}^{(+)}(N)\) and the total number of these paths \((N - 2)\) also is seen. The fact that both \(G_{(2)}(2)\) and \(E_{(4)}^{(+)}(2)\) vanish for butadiene \((N=2)\) containing no CP(3)s causes no surprise here. By contrast, the alternating signs of elements when passing from one line of the matrix \(G'_{(1)}(N)\) of Eq.(15) to another gives birth to a zero matrix \(G'_{(2)}(N)\) for dendralenes in accordance with absence of CP(3)s in these hydrocarbons. As a result, the stabilizing component of the fourth order energy \(E_{(4)}^{(+)\gamma}(N)\) also vanishes.

Proportionality between the number of non-zero elements of the matrix \(G_{(2)}\) and that of CP(3)s deserves more illustration. To this end, let us consider the four isomers of octatetraene I-IV (Fig. 1). The matrix \(G_{(2)}(I)\) and the energy increment \(E_{(4)}^{(+)}(I)\) of the linear system I result directly from Eq.(16) for \(N=4\), and \(E_{(4)}^{(+)}(I)\) equals to \(16\gamma^4/64\). The remaining formulae under our interest are as follows

\[
G_{(2)}(II) = \gamma^2 \frac{16}{16}, \quad G_{(2)}(III) = \gamma^2 \frac{16}{16}, \quad G_{(2)}(IV) = 0,
\]

\[
E_{(4)}^{(+)}(II) = \frac{16\gamma^4}{64}, \quad E_{(4)}^{(+)}(III) = \frac{8\gamma^4}{64}, \quad E_{(4)}^{(+)}(IV) = 0.
\]

Thus, total numbers of non-zero elements of matrices \(G_{(2)}\) coincide with two-fold numbers of CP(3)s for these systems too, i.e. with 4, 4, 2 and 0 for isomers I-IV, respectively. Moreover, the related energy components \((E_{(4)}^{(+)}\)) also are proportional to the same numbers.
Therefore, a simple relation may be concluded between elements of matrices $G_{(1)}$ and $G_{(2)}$, on the one hand, and the conjugated paths CP(2) and CP(3), on the other hand. Moreover, these CPs are the only conjugated fragments participating in the formation of elements concerned. Additivity of the consequent energetic increments $\mathcal{E}_{(2)}$ and $\mathcal{E}_{(4)}^{(+)}$ with respect to transferable contributions of CP(2)s and CP(3)s, respectively, also is among conclusions here.

Such a simple state of things, however, is no longer preserved when passing to terms of higher orders. To demonstrate this, we are about to consider elements of the matrix $G_{(3)}^{o}$ separately.

### 3.2 Analysis of elements of the third order matrix $G_{(3)}^{o}$

Let us start with the above-discussed linear polyene containing $N - 3$ CP(4)s, where $N \geq 3$. The respective common third order matrix $G_{(3)}^{o}(N)$ and the related sixth order energy increment $\mathcal{E}_{(6)}^{(+)}(N)$ follow from Eqs.(8), (12) and (16), viz.

$$G_{(3)}^{o}(N) = \begin{vmatrix} 0 & 1 & 0 & 2 & 0 & 0 & \ldots \\ -1 & 0 & 2 & 0 & 2 & 0 & \ldots \\ 0 & -2 & 0 & 2 & 0 & 2 & \ldots \\ -2 & 0 & -2 & 0 & 2 & 0 & \ldots \\ 0 & -2 & 0 & -2 & 0 & 2 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix}, \quad \mathcal{E}_{(6)}^{(+)}(N) = \frac{4\gamma^6[4(N - 3) + 1]}{256}. \tag{18}$$

where $-\gamma^3/32$ serves here and below as the standard factor for matrices $G_{(3)}^{o}$. Accordingly, $\gamma^6/256$ will be used as the ”subsidiary” sixth order energy unit. The first representatives of the series of matrices $G_{(3)}^{o}(N)$ and of energy increments $\mathcal{E}_{(6)}^{(+)}(N)$ corresponding to $N=3$ and 4 also deserve exhibiting, viz.

$$G_{(3)}^{o}(3) = \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix}, \quad G_{(3)}^{o}(4) \equiv G_{(3)}^{o}(I) = \begin{vmatrix} 0 & 1 & 0 & 2 \\ -1 & 0 & 2 & 0 \\ 0 & -2 & 0 & 1 \\ -2 & 0 & -1 & 0 \end{vmatrix}, \quad \mathcal{E}_{(6)}^{(+)}(3) = \frac{4\gamma^6}{256}, \quad \mathcal{E}_{(6)}^{(+)}(4) \equiv \mathcal{E}_{(6)}^{(+)}(I) = \frac{20\gamma^6}{256}. \tag{19}$$

These particular cases evidently represent linear isomers of hexatriene and of octatetraene I, respectively [Note that the energy increment $\mathcal{E}_{(6)}^{(+)}(3)$ follows directly from Eq.(18) after substituting $N=3$, but it is not the case for $G_{(3)}^{o}(3)$. A more detailed discussion of this point may be found in Ref.[15]. As is seen from Eq.(18),
the energy increment $\mathcal{E}_{(6)}^{(+)}(N)$ contains a dependence upon the number of CP(4)s of the given chain $(N - 3)$ in accordance with the expectation. The total number of non-zero elements of the matrix $G^o_{(3)}(N)$, however, exceeds the two-fold number of CP(4)s considerably. Moreover, significant elements correspond not only to BOs of third-neighbouring C=C bonds (as it may be expected on the basis of the above experience), but also to orbitals of their first-neighbouring pairs. For example, the matrix $G^o_{(3)}(4)[G^o_{(3)}(I)]$ contains eight non-zero elements referring to BOs of C=C bonds under numbers (1,2), (1,4), (2,3) and (3,4) (Fig.1), and the elements concerned take non-uniform values in addition, e. g. 2 and 1 for pairs of BOs (+)1, (+)4 and (−)1, (−)2, respectively. It is evident that all the above-enumerated elements contribute to the stabilizing increment $\mathcal{E}_{(6)}^{(+)}(N)$. Finally, neither the matrix $G^o_{(3)}(3)$ itself nor the relevant energy correction $\mathcal{E}_{(6)}^{(+)}(3)$ vanish for the three-membered system of hexatriene $(N = 3)$ containing no CP(4)s [in contrast to the zero matrix $G_{(2)}(2)$ and the vanishing correction $\mathcal{E}_{(4)}^{(+)}(2)$ of butadiene $(N = 2)$ discussed in the previous subsection].

To clarify the origin of these distinctive results, let us write down explicit expressions for elements of the matrix $G^o_{(3)}(4)[G^o_{(3)}(I)]$. Using the first relation of Eq.(12), we obtain

$$
G^o_{(3)14}(I) = -\frac{1}{2}S_{12}G_{(2)24} - G_{(2)13}Q_{34},
$$

$$
G^o_{(3)23}(I) = -\frac{1}{2}S_{21}G_{(2)13} - G_{(2)24}Q_{43},
$$

$$
G^o_{(3)12}(I) = \frac{1}{2}G_{(2)13}Q_{32}, \quad G^o_{(3)34}(I) = -\frac{1}{2}S_{32}G_{(2)24}. \quad (20)
$$

As is seen from the first formula of Eq.(20), a simple linear pathway from the BBO of the bond $C_1=C_5$ ($\varphi_{(+)}1$) to the ABO of the $C_4=C_8$ ($\varphi_{(-)}4$) underlies the element $G^o_{(3)14}(I)$. Moreover, mediating effects of intervening orbitals ($\varphi_{(+)}2$ and $\varphi_{(-)}3$) may be easily shown to be added together here. As a result, the absolute value of the element concerned coincides with 2. Thus, a simple relation may be concluded immediately between the element $G^o_{(3)14}(I)$ and the only CP(4) of the system I. A similar addition of contributing components takes place in the expression for the element $G^o_{(3)23}(I)$ too and the resulting value coincides with that of $G^o_{(3)14}(I)$. The underlying pathways, however, differ from linear ones in the latter case. Indeed, pathways over BOs con-
taining self-returning segments correspond to both components of the expression for $G_{(3)23}^o(I)$, wherein orbitals of terminal bonds ($\varphi(+)_1$ and $\varphi(-)_4$) participate as mediators. Meanwhile, orbitals of the fourth ($C_4=C_8$) and first ($C_1=C_5$) bonds play no role in the formation of the first and second component of the element $G_{(3)23}^o(I)$, respectively. It is evident that conjugated paths $CP(3)$ embracing triplets of C=C bonds under numbers 1,2,3 and 2,3,4 may be correspondingly ascribed to the above-specified components. The same refers also to elements $G_{(3)12}^o(I)$ and $G_{(3)34}^o(I)$.

We may expect, therefore, that matrices $G_{(3)}^o$ generally contain information not only about $CP(4)$s of the given polyene, but also about shorter conjugated paths. It is also likely that the presence of a standard $CP(4)$ is not among necessary conditions for a non-zero matrix $G_{(3)}^o$ to represent a certain pi-electron system. To support these anticipations, let us consider some polyenes of more involved constitutions.

Let us start with the isomer of octatetraene III (Fig. 1) containing both conjugated and cross-conjugated fragments. As opposed to its linear counterpart I, the new isomer III contains no $CP(4)$. Nevertheless, it is characterized by a non-zero matrix $G_{(3)}^o(III)$ and a significant energy increment $E_{(6)}^{(+)}(III)$, viz.

\[
G_{(3)}^o(III) = -\gamma^3 32 \begin{vmatrix}
0 & 0 & 0 & -1 \\
0 & 0 & -1 & 0 \\
0 & 1 & 0 & -1 \\
1 & 0 & 1 & 0
\end{vmatrix}, \quad E_{(6)}^{(+)}(III) = \frac{6\gamma^6}{256}.
\] (21)

Moreover, elements $G_{(3)14}^o$ and $G_{(3)41}^o$ take non-zero values in the matrix $G_{(3)}^o(III)$ in spite of the fact that the terminal C=C bonds ($C_1=C_5$ and $C_4=C_8$) are not joined by a conjugated path. This result causes little surprise if we recall the definition of the matrix $G_{(3)}^o$ in terms of $G_{(2)}$ shown in Eq.(12). Indeed, this definition indicates non-zero values of elements $S_{12}$ and $G_{(2)24}$ to be sufficient to ensure a significant element $G_{(3)14}^o$ and this condition is met by the terminal orbitals $\varphi(+)_1$ and $\varphi(-)_4$ of our system III. Again, some similarity is beyond any doubt between constitutions of matrices $G_{(3)}^o(I)$ of Eq.(19) and $G_{(3)}^o(III)$ of Eq.(21). These two points allow the isomer III to be considered as a partially conjugated system. In this connection, a new concept of the semi-conjugated path may be introduced that contributes to the sixth order stabilization of the system along with the usual $CP(4)$s. In the present case, we will have to do with a semi-conjugated path embracing four C=C bonds.
and abbreviated below by SCP(4). The lower stabilizing effect of this new path as compared to the standard increment of the only CP(4) of the linear isomer I (see Eq.(19)) causes no surprise here.

Another important distinction between the third order matrices $G_{(3)}^o$ along with the related energy increments $\mathcal{E}^{(+)}_{(6)1}$ and their counterparts of lower orders (Subsect. 3.1) consists in much more involved dependences of the third (sixth) order characteristics upon the numbers of the standard conjugated paths when passing from linear to branched polyenes. This distinction may be traced back to the fact that the side subchains of branched systems offer new self-returning segments for pathways underlying separate elements $G_{(3)i}^o (G_{(3)i}^o)$ and thereby the absolute values of these elements become excessively increased. For example, the branched octatetraene II is characterized by the following matrix $G_{(3)}^o (II)$ and the energy increment $\mathcal{E}^{(+)}_{(6)1} (II)$:

$$G_{(3)}^o (II) = -\frac{\gamma^3}{32} \left| \begin{array}{cccc}
0 & 2 & 0 & 0 \\
-2 & 0 & 1 & 1 \\
0 & -1 & 0 & 0 \\
0 & -1 & 0 & 0 \\
\end{array} \right|, \quad \mathcal{E}^{(+)}_{(6)1} (II) = \frac{12\gamma^6}{256}. \tag{22}$$

It is seen that absolute values of elements $G_{(3)12}^o (II)$ and $G_{(3)21}^o (II)$ coincide with $G_{(3)14}^o (I)$ and $G_{(3)23}^o (I)$ of Eq.(19) in spite of absence of CP(4)s in the branched system II. These increased elements are unambiguously related to emergence of two self-returning segments in the pathways over BOs underlying elements $G_{(3)12}^o (II)$ and $G_{(3)21}^o (II)$, namely of segments embracing the bonds $C_4=C_8$ and $C_3=C_7$. Nevertheless, the total value of the stabilizing increment $\mathcal{E}^{(+)}_{(6)1} (II)$ is almost two times smaller for the branched isomer II as compared to the relevant value $(20\gamma^6/256)$ for its linear counterpart I.

The decisive role of the side subchains in the formation of matrices $G_{(3)}^o$ (and thereby of energy components $\mathcal{E}^{(+)}_{(6)1}$) may be further illustrated by comparing these characteristics for isomers of decapentaene V, VI and IX (Fig. 2), where $N=5$. The total numbers of CP(4)s correspondingly equal to 2, 2 and 1 in these systems. Again, the isomers concerned may be regarded as consisting of the principal linear chain and of a side subchain, embracing the $C=C$ bonds under numbers 1-4 and 5, respectively. The side subchain ($C_5=C_{10}$) then takes distinct positions with respect to the principal chain in the systems under comparison and thereby it offers different sets of self-
Isomers of decapentaene (V-XI) containing five C=C bonds (N=5). Numberings of these bonds also are shown.

Figure 2: Isomers of decapentaene (V-XI) containing five C=C bonds (N=5). Numberings of these bonds also are shown.

returning segments for pathways over BOs underlying particular elements of matrices $G_o^{(3)}(V)$, $G_o^{(3)}(VI)$ and $G_o^{(3)}(IX)$. As a result, distinctions may be anticipated both in the constitutions of the above-enumerated matrices and in values of the consequent energy components.

To demonstrate this, let us start with matrices $G_o^{(3)}$. The matrix $G_o^{(3)}(V)[G_o^{(3)}(5)]$ easily results from the general expression of Eq.(18) and contains eight elements equal to either 2 or -2 and four elements coinciding with either 1 or -1. Meanwhile, the remaining matrices and the consequent energy increments are as follows

$$G_o^{(3)}(VI) = -\frac{\gamma^3}{32} \begin{vmatrix} 0 & 1 & 0 & 2 & 2 \\ -1 & 0 & 3 & 0 & 0 \\ 0 & -3 & 0 & 1 & 1 \\ -2 & 0 & -1 & 0 & 0 \\ -2 & 0 & -1 & 0 & 0 \end{vmatrix}, \quad G_o^{(3)}(IX) = -\frac{\gamma^3}{32} \begin{vmatrix} 0 & 2 & 0 & 2 & 0 \\ -2 & 0 & 2 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 \\ -2 & 0 & -1 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 \end{vmatrix},$$

$$E_{(6)1}^{(+)}(V) = -\frac{36\gamma^6}{256}, \quad E_{(6)1}^{(+)}(VI) = \frac{40\gamma^6}{256}, \quad E_{(6)1}^{(+)}(IX) = \frac{30\gamma^6}{256}. \quad (23)$$

It is seen that the matrix $G_o^{(3)}(VI)$ contains elements of higher absolute values as compared to $G_o^{(3)}(IX)$ and $E_{(6)1}^{(+)}(VI)$ accordingly exceeds $E_{(6)1}^{(+)}(IX)$. This result is in line with distinct numbers of CP(4)s in the isomers VI and IX (2 and 1) and thereby causes little surprise. It deserves adding, however, that the energy component $E_{(6)1}^{(+)}(IX)$ does not coincide with $E_{(6)1}^{(+)}(I)$ of Eq.(19) in spite of the same number of CP(4)s in the systems I and IX (equal to 1). Comparison of matrices $G_o^{(3)}(V)$ and $G_o^{(3)}(VI)$ yields even more unexpected conclusions. Indeed, the matrix $G_o^{(3)}(VI)$
differs from $G_{(3)}^o(V)$ significantly in spite of the same number of CP(4)s present in both systems. Moreover, the sum of squares of elements of the former matrix exceeds that of the latter and, consequently, the branched isomer VI proves to be described by a higher energy increment $E_{(6)}^{(+)}$ as compared to its linear counterpart (V). This result implies a dependence of the sixth order energy upon the mutual arrangement of the two CP(4)s [Note that an increased overall stability of the branched system VI vs. the linear one (V) is not among the implications as discussed in Sect. 4].

In summary, a relation is beyond any doubt between the third order matrix $G_{(3)}^o$ representing a certain polyene and the number of CP(4)s present there as it was the case with matrices $G_{(1)}$ and $G_{(2)}$ determined by numbers of CP(2)s and CP(3)s, respectively (Subsect. 3.1). In contrast to the latter cases, however, the total number of CP(4)s is not the only factor determining the given matrix $G_{(3)}^o$ and thereby the consequent energy increment $E_{(6)}^{(+)}$: Other details of constitution of the given system also play their role here, e.g. presence of semi-conjugated paths (SCP(4)s) and a particular mutual arrangement of several CP(4)s (if any).

Let us turn now to elements of matrix products of Eqs.(3) and (9)–(11).

### 3.3 The role of composite conjugated paths in the formation of elements of matrix products

Let us start with the product $G_{(1)}G_{(1)}^+$ determining the fourth order destabilizing energy component $E_{(4)}^{(-)}$ of Eq.(3). It is evident that an element $(G_{(1)}G_{(1)}^+)^{ij}$ does not vanish if in the given system there is an ABO $\varphi_{(-)l}$ such that $G_{(1)il} \neq 0$ and $G_{(1)lj}^{+} \equiv G_{(1)jl} \neq 0$. Because of the equality $G_{(1)ii} = 0$ for any $i$ (see Eq.(7)), ABOs $\varphi_{(-)i}$ and $\varphi_{(-)j}$ are not able to play this role. Thus, the ABO $\varphi_{(-)l}$ necessarily belongs to a third (say Lth) C=C bond, where L $\neq$ I and L $\neq$ J. In other words, two simple mutually connected pathways are required here, namely a pathway from $\varphi_{(+)}^{(1)i}$ to $\varphi_{(-)}^{(1)l}$ and that from $\varphi_{(-)}^{(1)i}$ and $\varphi_{(+)}^{(1)j}$. Since a CP(2) corresponds to any element $G_{(1)il}$ (Subsect. 3.1), the above condition resolves itself into a requirement of two simple CP(2)s embracing a common (Lth) C=C bond. Given that this is the case, we will say that in the given system there is a composite conjugated path over three C=C bonds abbreviated below by CCP(3). Besides, a CCP(3) is automatically ensured under
presence of a standard CP(3), but not vice versa (see Sect. 4). Further, the matrix product \( G_{(1)}G_{(1)}^+ \) is characterized by non-zero diagonal elements \((G_{(1)}G_{(1)}^+)_i\) that are interpretable as indirect self-interactions of respective BBOs \( \varphi_{(+)}i \) via ABOs of the neighbouring C=C bonds (Sect. 2). In this connection, let us also define self-returning composite conjugated paths coinciding with squares of CP(2)s. As with the latter, these new paths also embrace pairs of neighbouring C=C bonds. Thus, let us use the abbreviation SRCCP(2). On the whole, the matrix \( G_{(1)}G_{(1)}^+ \) of a certain polyene may be then expected to contain information about both CCP(3)s and SRCCP(2)s.

For illustration, let us consider matrices \( G_{(1)}G_{(1)}^+ \) representing the linear octate-traene (I), as well as its branched and cross-conjugated isomers II and IV (Fig. 1). The first two matrices under comparison differ one from another significantly, especially in respect of diagonal elements, viz.

\[
G_{(1)}G_{(1)}^+(I) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & -1 & 0 \\ 0 & 2 & 0 & -1 \\ -1 & 0 & 2 & 0 \\ 0 & -1 & 0 & 1 \end{vmatrix},

\quad G_{(1)}G_{(1)}^+(II) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & -1 & -1 \\ 0 & 3 & 0 & 0 \\ -1 & 0 & 1 & 1 \\ -1 & 0 & 1 & 1 \end{vmatrix}.
\]

(24)

The reason for this distinction consists in the increased number of first neighbours of the second \( (C_2=C_6) \) bond in the branched isomer II and thereby in the larger indirect self-interaction of the relevant BBO \( \varphi_{(+)}2 \). In terms of conjugated paths we have to do here with an increased number of SRCCP(2)s referring to the 2nd C=C bond. If we recall here that isomers I and II both contain two CP(3)s, the above result becomes even more important in distinguishing between their stabilities (Sect. 4). So far as the matrix \( G_{(1)}G_{(1)}^+(IV) \) is concerned, it resembles \( G_{(1)}G_{(1)}^+(I) \) in respect of absolute values of all matrix elements [negative off-diagonal elements of \( G_{(1)}G_{(1)}^+(I) \) become replaced by positive ones when passing to \( G_{(1)}G_{(1)}^+(IV) \)]. This implies the linear isomer I and the cross-conjugated one IV to contain the same sets of both linear and self-returning composite conjugated paths (i.e. of CCP(3)s and SRCCP(2)s) in spite of different numbers of the standard CP(3)s (2 and 0).

Let us turn now to third order matrix products and start with \( G_{(1)}G_{(1)}^+G_{(1)} \). The skew-symmetric (skew-Hermitian) nature of this matrix (Sect. 2) implies zero values for any diagonal element \((G_{(1)}G_{(1)}^+G_{(1)})_{ii}\). Nevertheless, an analogy still exists
between products $G_{(1)}G_{(1)}^+G_{(1)}$ and $G_{(1)}G_{(1)}^+$. In particular, the matrix $G_{(1)}G_{(1)}^+G_{(1)}$ may be similarly shown to represent products of three connected CP(2)s, the total number of the embraced C=C bonds generally coinciding with four. Accordingly, we may define composite conjugated paths over four C=C bonds (CCP(4)s). It should be mentioned, however, that the overall situation becomes somewhat more involved when passing from $G_{(1)}G_{(1)}^+$ to $G_{(1)}G_{(1)}G_{(1)}^+$, as it was the case when comparing matrices $G_{(2)}$ and $G_{(3)}^o$ (Sect. 3). In particular, pathways over BOs underlying elements $(G_{(1)}G_{(1)}^+G_{(1)})_d$ may possess self-returning segments (as it was the case with $G_{(3)i}^o$). Consequently, the resulting CCPs actually embrace three or even two C=C bonds. It is also evident that zero diagonal elements of the product $G_{(1)}G_{(1)}^+G_{(1)}$ reflect impossibility of completely self-returning paths in this case. Finally, matrix products $G_{(1)}G_{(2)}^+$ and $G_{(2)}G_{(1)}^+$ remain to be discussed. In contrast to previous cases, these products are neither symmetric (Hermitian) nor skew-symmetric (skew-Hermitian) matrices. It is evident that the underlying CCPs consist of products of a CP(2) and a CP(3), and of a CP(3) and a CP(2), respectively, and also generally embrace four C=C bonds. Self-returning segments are possible here too.

It is seen, therefore, that elements of matrix products are determined by conjugated paths of a non-standard (viz. composite) nature. Moreover, most of these new paths give birth to destabilizing energy components (e.g. $\mathcal{E}_{(4)}^{(-)}$ and $\mathcal{E}_{(6)}^{(-)}$).

Before finishing this Section, the following remark deserves to be made: Energy increments originating from matrix products $G_{(1)}G_{(1)}^+, G_{(1)}G_{(2)}^+$, etc. and these related to simple matrices $G_{(1)}, G_{(2)}$ and $G_{(3)}^o$ hardly are independent. Quite the reverse, a certain interdependence may be foreseen between some of these increments, e.g. between $\mathcal{E}_{(6)}^{(+)}$ and $\mathcal{E}_{(6)}^{(-)}$. The main reason for such an anticipation consists in the presence of the same matrix $G_{(2)}$ in the definitions of underlying matrices $G_{(3)}^o$ and $G_{(1)}G_{(2)}^+$ (see Eq.(12)). [Besides, both matrices $G_{(3)}^o$ and $G_{(1)}G_{(2)}^+$ vanish, if $G_{(2)}$ coincides with a zero matrix]. Thus, an increased stabilization of a certain system due to a larger increment $\mathcal{E}_{(6)}^{(+)}$ may be expected to be accompanied by a growing destabilization ($\mathcal{E}_{(6)}^{(-)}$) and vice versa. Given that relative stabilities of different isomers are under interest (Sect. 4), the outcome of the comparison then depends on the overall balance between energy increments of opposite signs.
4 Discussions of relative stabilities of specific isomers

Let us start with comparison of linear polyenes to their cross-conjugated isomers (dendralenes) in respect of overall relative stabilities of their pi-electron systems. Zero order energies of these isomers are uniform for the same number of C=C bonds (N), viz. $E_{(0)}(N) = E'_{(0)}(N) = 2N$. The relevant second order increments also coincide one with another (see the implications of Eq.(15)). Finally, the stabilizing components of the fourth order energies are discussed in the Subsect. 3.1 [$E_{(4)}^{(+)}(N)$ is shown in Eq.(16) and takes a significant value because of N-2 three-membered conjugated paths (CP(3)s) present in the linear system, whereas $E_{(4)}'\left( ^{(-)} \right)(N)$ vanishes due to absence of these paths in dendralenes]. Thus, let us turn immediately to the remaining (destabilizing) components of the fourth order energies.

Employment of the expression for the matrix $G_{(1)}(N)$ of Eq.(15) to construct the product $(G_{(1)} G^+_{{(1)}})(N)$ shows this important representation of linear polyenes to contain elements 1,2,2...2,1 in its principal diagonale along with $-1$ in the second-neighbouring off-diagonal positions [The matrix $(G_{(1)} G^+_{{(1)}})(I)$ of Eq.(24) serves as an example for N=4]. Moreover, the analogous matrix product $(G_{(1)} G^+_{{(1)}})'(N)$ representing the dendralene series and originating from $G'_{(1)}(N)$ of Eq.(15) also closely resembles the above-discussed one, except for opposite (i.e. positive) signs of all off-diagonal elements. Accordingly, destabilizing components of fourth order energies are uniform for both systems under comparison. The latter result may be entirely traced back to an evident fact that products of CP(2)s and thereby numbers of composite conjugated paths CCP(3)s coincide one with another in both polyenes. The relevant total fourth order energies are then as follows

$$E_{(4)}(N) = \frac{2\gamma^4(N-3)}{64}, \quad E'_{(4)}(N) = E'^{(-)}_{(4)}(N) = E^{(-)}_{(4)}(N) = -\frac{\gamma^4[6(N-2) + 2]}{64}, \quad (25)$$

where $E_{(4)}^{(+)}(N)$ is taken from Eq.(16). It is seen that the correction $E_{(4)}(N)$ is a positive quantity for $N \geq 4$ owing to predominance of its stabilizing component $E_{(4)}^{(+)}(N)$ over the destabilizing one $E_{(4)}^{(-)}(N)$. This implies the sufficiently long linear polyenes to be additionally stabilized vs. the sum $E_{(0)}(N) + E_{(2)}(N)$ due to the fourth order energy. By contrast, the analogous correction of dendralenes ($E'_{(4)}(N)$) consists of the
destabilizing component only and, consequently, it is a negative quantity [Particular cases of Eq.(25) referring to $N=2$ and $N=3$ also are of interest. In the case of butadiene ($N=2$), both relations yield the same correction $E_{(4)}(2)$ equal to $-2\gamma^4/64$ in accordance with the expectation, which is a negative quantity in addition due to absence of CP(3)s. This correction consists of the destabilizing component only that originates from SRCCP(2)s. For the linear hexatriene ($N=3$), the two components ($E_{(4)}^{(+)}(3)$ and $E_{(4)}^{(-)}(3)$) cancel out one another and the total fourth order energy takes a zero value. The branched isomer of hexatriene, in turn, is characterized by a negative fourth order energy].

Thus, a higher relative stability of linear polyenes vs. dendralenes unambiguously follows from our results and this conclusion coincides with those of other approaches [32-35]. As with the standard model of conjugated paths [5], the above analysis also indicates the presence of CP(3)s to be the origin of the increased stability of linear isomers. In contrast to the standard model, however, an additional destabilizing factor is now revealed to manifest itself in both systems under comparison that is interpretable as a contribution of composite conjugated paths. Only because of the above-established coincidence of absolute values of the underlying energy increments for linear and cross-conjugated systems, the destabilizing factor becomes irrelevant when comparing their relative stabilities.

For other series of polyenes (e.g. the branched ones), a general analysis like that carried out above hardly is feasible. Thus, we will confine ourselves to comparisons of relative stabilities of individual representatives of different series.

Let us start with the four isomers of octatetraene I-IV (Fig.1) containing the same number of C-C bonds and thereby of CP(2)s (equal to 3). Accordingly, the relevant second order energies also are uniform. Again, the total numbers of CP(3)s correspondingly coincide with 2, 2, 1 and 0 for systems I-IV. Since the linear isomer (I) and its cross-conjugated analogue (IV) are particular cases of the above-considered polyenes, Eq.(25) yields $E_{(4)}(I)$ and $E_{(4)}(IV)$ equal to $2\gamma^4/64$ and $-14\gamma^4/64$, respectively.

Let us now dwell on the branched isomer II. The stabilizing component of the fourth order energy $E_{(4)}^{(+)}(II)$ is shown in Eq.(17) and coincides with $E_{(4)}^{(+)}(I)$ following
from Eq.(16) for N=4 owing to similar non-zero elements of matrices \( G_{(2)}(II) \) and \( G_{(2)}(I) \) (Subsect. 3.1). This result is in line with the same number of CP(3)s in polyenes I and II. Meanwhile, the matrix \( G_{(1)}G_{(1)}^{+}(II) \) differs from both \( G_{(1)}G_{(1)}^{+}(I) \) and \( G_{(1)}G_{(1)}^{+}(IV) \) significantly (see Eq.(24) and the discussion nearby). It is evident that the sum of squares of elements of the matrix \( G_{(1)}G_{(1)}^{+}(II) \) exceeds the relevant value for isomers I and IV. As a result, the destabilizing component \( \varepsilon_{(4)}^{(-)}(II) \) is of an increased absolute value vs. \( \varepsilon_{(4)}^{(-)}(I) \) and \( \varepsilon_{(4)}^{(-)}(IV) \). The overall result referring to the isomer II is then as follows

\[
\varepsilon_{(4)}^{(+)}(II) = \frac{16\gamma^4}{64}, \quad \varepsilon_{(4)}^{(-)}(II) = -\frac{18\gamma^4}{64}, \quad \varepsilon_{(4)}(II) = -\frac{2\gamma^4}{64}. \tag{26}
\]

Hence, the total fourth order energies \( \varepsilon_{(4)}(I) \) and \( \varepsilon_{(4)}(II) \) differ one from another for isomers I and II in spite of the same numbers of CP(3)s. Moreover, the linear isomer is predicted to be more stable as compared to the branched one (II). Although this result is in line with predictions of the standard CP model (as well as with the relevant general graph-theoretical results [34,35]), the above analysis indicates another underlying reason. Indeed, the branched isomer II is now concluded to be less stable owing to a greater destabilizing effect of self-returning composite conjugated paths (SRCCP(2)s) defined in Sect. 3. Meanwhile, the greater stability of the isomer I (vs. the branched analogue II) is traced back to the presence of a CP(4) in the linear chain when the usual model of conjugated paths is applied.

Finally, the semi-conjugated isomer (III) remains to be discussed. The relevant matrix \( G_{(2)}(III) \) is shown in Eq.(17) and contains two non-zero elements in accordance with a single CP(3) present in the given system. Meanwhile, the matrix \( G_{(1)}G_{(1)}^{+}(III) \) closely resembles \( G_{(1)}G_{(1)}^{+}(I) \) of Eq.(24) in respect of absolute values of non-zero elements. We then obtain

\[
\varepsilon_{(4)}^{(+)}(III) = \frac{8\gamma^4}{64}, \quad \varepsilon_{(4)}^{(-)}(III) = -\frac{14\gamma^4}{64}, \quad \varepsilon_{(4)}(III) = -\frac{6\gamma^4}{64}. \tag{27}
\]

Thus, the above results indicate the following order of relative stabilities of isomers:

\( I > II > III > IV \). Completely similar conclusions follow also for analogous isomers of decapentaene V, VI, VII and VIII shown in Fig. 2. The relevant fourth order energies correspondingly coincide with \( 4\gamma^4/64 \), 0, \( -4\gamma^4/64 \) and \( -12\gamma^4/64 \).
the above-concluded relative orders of stability for both I-IV and V-VIII are in line with the maximal $\pi$− energy of 1,1-divinyl isomers of polyenes among the branched ones established in Ref. [35].

It is seen, therefore, that fourth order energies are sufficient to distinguish between relative stabilities of representatives of different principal series of polyenes. In the case of distinct isomers characterized by more similar overall constitutions, however, the fourth order energies often are uniform and, consequently, sixth order corrections should be invoked. Let turn now to relevant examples.

Let us start with comparison of the above-discussed isomers of decapentaene VI and IX containing the same number of CP(3)s equal to three. As it may be easily proven after constructing the relevant principal matrices, a zero fourth order energy is peculiar to both isomers under comparison and this result evidently causes little surprise. Again, distinct numbers of CP(4)s (namely 2 and 1 for systems VI and IX, respectively) allow us to expect the sixth order energies to be responsible for different stabilities of these isomers (Subsect. 3.2). Thus, let us now turn to corrections $\mathcal{E}^{(+)}_{(6)}(VI)$ and $\mathcal{E}^{(+)}_{(6)}(IX)$.

Matrices $\mathbf{G}^0_{(3)}(VI)$ and $\mathbf{G}^0_{(3)}(IX)$ along with the consequent energy increments $\mathcal{E}^{(+)}_{(6)}(VI)$ and $\mathcal{E}^{(+)}_{(6)}(IX)$ are shown in Eq.(23) and discussed nearby. A higher value of $\mathcal{E}^{(+)}_{(6)}(VI)$ vs. $\mathcal{E}^{(+)}_{(6)}(IX)$ was in line with the relevant numbers of CP(4)s. Further, matrices $\mathbf{G}_{(1)} \mathbf{G}^+_{(1)} \mathbf{G}_{(1)}(VI)$ and $\mathbf{G}_{(1)} \mathbf{G}^+_{(1)} \mathbf{G}_{(1)}(IX)$ determining the second stabilizing increments $\mathcal{E}^{(+)}_{(6)2}(VI)$ and $\mathcal{E}^{(+)}_{(6)2}(IX)$, respectively, prove to be similar in respect of absolute values of their non-zero elements. This implies the numbers of the relevant composite conjugated paths (consisting of three CP(2)s) to be uniform in the isomers VI and IX. As a result, energy increments $\mathcal{E}^{(+)}_{(6)2}(VI)$ and $\mathcal{E}^{(+)}_{(6)2}(IX)$ also coincide one with another and equal to $40 \gamma^6/256$.

As with the above-discussed matrices $\mathbf{G}^0_{(3)}(VI)$ and $\mathbf{G}^0_{(3)}(IX)$ of Eq.(23), the matrix $\mathbf{G}_{(1)} \mathbf{G}^+_{(2)}(VI)$ also contains more non-zero elements as compared to $\mathbf{G}_{(1)} \mathbf{G}^+_{(2)}(IX)$ [Apart from a single element equal to 2, these matrices involve eight and seven elements, respectively, that are equal to either 1 or $-1$. This result is in line with the above-foreseen parallelism between alterations in elements of matrices $\mathbf{G}^0_{(3)}$ and $\mathbf{G}_{(1)} \mathbf{G}^+_{(2)}$ (see the last paragraph of Sect. 3)]. Consequently, the absolute value of the
sixth order destabilizing increment $E_{(6)}^{(-)}(VI)$ also exceeds that of $E_{(6)}^{(-)}(IX)$. Moreover, the same refers also to increments $E_{(6)}^{(u)}(VI)$ and $E_{(6)}^{(u)}(IX)$, viz.

$$E_{(6)}^{(-)}(VI) = -\frac{96\gamma^6}{256}, \quad E_{(6)}^{(-)}(IX) = -\frac{88\gamma^6}{256}, \quad E_{(6)}^{(u)}(VI) = \frac{16\gamma^6}{256}, \quad E_{(6)}^{(u)}(IX) = \frac{8\gamma^6}{256}.$$  

As is seen after summing up the relevant contributions, the sixth order stabilization energy increases by $18\gamma^6/256$, whereas the absolute value of destabilization grows only by $8\gamma^6/256$ when passing from IX to VI. The total sixth order energies then coincide with zero and $-10\gamma^6/256$ for isomers VI and IX, respectively, and indicate the former pi-electron system to be more stable than the latter in accordance with graph-theoretical conclusions of Ref.[35]. The present result may be traced back to the relevant numbers of CP(4)s. The relation between these numbers and relative stabilities of isomers VI and IX, however, is far from being of a straightforward nature as the above discussion shows.

Let us return again to the semi-conjugated isomer of decapentaene (VII) and compare it to a similar one (X) (Fig. 2). As with the above-considered couple (VI and IX), the isomers VII and X also are characterized by the same numbers of CP(3)s and, consequently, by uniform fourth order energies equal to $-4\gamma^4/64$. Different numbers of CP(4)s of these hydrocarbons also deserve mention here (these coincide with 1 and 0 for isomers VII and X, respectively). Thus, let us turn to the sixth order energies $E_{(6)}(VII)$ and $E_{(6)}(X)$.

Matrices $G^{o}_{(3)}(VII)$ and $G^{o}_{(3)}(X)$ exhibit a clear parallelism between absolute values of their non-zero elements and the respective numbers of CP(4)s as previously. Accordingly, the total number of non-zero elements is higher in the matrix $G_{(1)}G_{(2)}^{+}(VII)$ as compared to $G_{(1)}G_{(2)}^{+}(X)$. Meanwhile, matrices $G_{(1)}G_{(1)}^{+}G_{(1)}(VII)$ and $G_{(1)}G_{(1)}^{+}G_{(1)}(X)$ contain analogous non-zero elements. The total sixth order energies $E_{(6)}(VII)$ and $E_{(6)}(X)$ then correspondingly equal to $2\gamma^6/256$ and $-8\gamma^6/256$. Thus, the isomer VII is predicted to be more stable as compared to X in analogy with the above-considered couple VI and IX. The decisive role of CP(4)s in the formation of this result also is beyond any doubt.

Let us now compare the semi-conjugated system VIII to a closely related one (XI). These isomers also are characterized by coinciding numbers of CP(3)s and by uniform
fourth order energies (equal to $-12\gamma^4/64$). As opposed to previous examples, however, both VIII and XI contain no CP(4)s. This implies that the standard model of conjugated paths is not able to distinguish between their stabilities. Again, the same isomers VIII and XI differ one from another in numbers of semi-conjugated paths (SCP(4)s) defined in Sect. 3. Indeed, the system VIII contains a single SCP(4) embracing the C=C bonds under numbers 2,3,4,5. Meanwhile, the remaining isomer XI involves two SCP(4)s made up of C=C bonds 1,2,3,4 and 2,3,4,5. In this connection, comparison of sixth order energies of polyenes VIII and IX is of particular interest.

As with the above-considered couples of isomers, matrices $G_{(1)}G_{(1)}^+G_{(1)}(VIII)$ and $G_{(1)}G_{(1)}^+G_{(1)}(XI)$ contain uniform sets of non-zero elements and contribute coinciding increments to the relevant sixth order energies. Again, matrices $G_{(3)}^o(VIII)$ and $G_{(3)}^o(XI)$ correspondingly involve six and eight non-zero elements equal to either 1 or $-1$ and thereby reflect different numbers of SCP(4)s present in these systems. Consequently, the energy increments $E_{(6)}^{(+)}(VIII)$ and $E_{(6)}^{(+)}(XI)$ coincide with $6\gamma^6/256$ and $8\gamma^6/256$, respectively. Thus, $E_{(6)}^{(+)}(XI)$ exceeds $E_{(6)}^{(+)}(VIII)$ by $2\gamma^6/256$ in accordance with the expectation. Analogously, matrices $G_{(1)}G_{(2)}^+(VIII)$ and $G_{(1)}G_{(2)}^+(XI)$ contain three and four unit elements, respectively, and yield the following energy increments

$$E_{(6)}^{(-)}(VIII) = -\frac{24\gamma^6}{256}, \quad E_{(6)}^{(-)}(XI) = \frac{32\gamma^6}{256}, \quad E_{(6)}^{(u)}(VIII) = E_{(6)}^{(u)}(XI) = 0. \quad (29)$$

Thus, the absolute value of the destabilizing increment is increased by $8\gamma^6/256$ when passing from VIII to XI and this alteration exceeds that of the stabilizing increment considerably. It is no surprise in this connection that the isomer VIII proves to be more stable as compared to its counterpart XI [The total sixth order energies correspondingly equal to $10\gamma^6/256$ and $4\gamma^6/256$]. Such a somewhat unexpected result may be entirely traced back to the higher destabilizing effect of composite conjugated paths (CCP(4)s) underlying matrices $G_{(1)}G_{(1)}^+$ in the isomer XI vs. VIII.

The last example under our interest embraces four isomers XII, XIII, XIV and XV of Fig. 3, all of them containing six C=C bonds (N=6) and characterized by uniform fourth order energies $-6\gamma^4/64$ in addition. The total numbers of CP(3)s also are uniform here and coincide with 3. Meanwhile, the relevant numbers of the standard
Figure 3: Selected polyenes (XII-XV) containing six C=C bonds (N=6). Numberings of these bonds also are shown.

CP(4)s correspondingly equal to 0, 1, 1, and 2. This implies the isomers XIII and XIV to be of the same composition in terms of the standard conjugated paths. It is no surprise that these isomers have been never discriminated as concluded in Ref.[5]. The relevant numbers of SCP(4)s coincide with 3, 2, 1 and 1, respectively.

Separate increments to the sixth order energies of the above enumerated systems also follow the above-observed trends. Thus, the first stabilizing increments \(\mathcal{E}_{(6)}^{(+)}\) originating from matrices \(G_{(3)}^0\) are as follows

\[
\begin{align*}
\mathcal{E}_{(6)}^{(+)}(XII) &= \frac{22\gamma_6}{256}, \\
\mathcal{E}_{(6)}^{(+)}(XIII) &= \frac{34\gamma_6}{256}, \\
\mathcal{E}_{(6)}^{(+)}(XIV) &= \frac{32\gamma_6}{256}, \\
\mathcal{E}_{(6)}^{(+)}(XV) &= \frac{42\gamma_6}{256}, \\
\end{align*}
\]

and correlate with the total numbers of both CP(4)s and SCP(4)s. Furthermore, matrices \(G_{(1)} G_{(1)}^+ G_{(1)}\) are similar as previously except for the matrix \(G_{(1)} G_{(1)}^+ G_{(1)}(XIII)\) possessing a somewhat higher number of non-zero elements as compared to the remaining ones. The relevant energy increments take the form

\[
\begin{align*}
\mathcal{E}_{(6)}^{(+)}(XII) &= \mathcal{E}_{(6)}^{(+)}(XIV) = \mathcal{E}_{(6)}^{(+)}(XV) = \frac{50\gamma_6}{256}, \\
\mathcal{E}_{(6)}^{(+)}(XIII) &= \frac{53\gamma_6}{256}. \\
\end{align*}
\]

Finally, matrices \(G_{(1)} G_{(2)}^+\) contain different numbers of unit elements along with a single element 2, namely seven, nine, eight and nine unit elements for isomers XII-
XIV, respectively. These matrices give birth to following energy increments

\[
\begin{align*}
\mathcal{E}^{(-)}_{(6)}(XII) &= -\frac{88\gamma^6}{256}, \\
\mathcal{E}^{(-)}_{(6)}(XIII) &= \mathcal{E}^{(-)}_{(6)}(XV) = -\frac{104\gamma^6}{256}, \\
\mathcal{E}^{(-)}_{(6)}(XIV) &= -\frac{96\gamma^6}{256}, \\
\mathcal{E}^{(u)}_{(6)}(XII) &= 0, \\
\mathcal{E}^{(u)}_{(6)}(XIII) &= \mathcal{E}^{(u)}_{(6)}(XIV) = \frac{8\gamma^6}{256}, \\
\mathcal{E}^{(u)}_{(6)}(XV) &= \frac{16\gamma^6}{256}.
\end{align*}
\]  

(32)

It is seen that absolute values of destabilizing increments also correlate with total numbers of both CP(4)s and SCP(4)s in the isomers XII-XIV. After summing up all increments concerned, we obtain

\[
\begin{align*}
\mathcal{E}^{(-)}_{(6)}(XII) &= -\frac{16\gamma^6}{256}, \\
\mathcal{E}^{(-)}_{(6)}(XIII) &= \frac{9\gamma^6}{256}, \\
\mathcal{E}^{(-)}_{(6)}(XIV) &= -\frac{6\gamma^6}{256}, \\
\mathcal{E}^{(u)}_{(6)}(XV) &= \frac{4\gamma^6}{256}.
\end{align*}
\]  

(33)

Thus, the relative stability grows with the increasing number of the standard CP(4)s in this case too. Moreover, the isomers XIII and XIV (both containing a single CP(4)) also are discriminated when applying the perturbative approach: The isomer XIII is predicted to be less stable as compared to XIV as it was the case with XI vs. VIII.

5 Conclusions

Analysis of power series for total energies of \(\pi\)-electron systems of acyclic conjugated hydrocarbons (polyenes) supports the principal assumptions underlying the model of conjugated paths and thereby offers a justification of the latter. In this respect, the following points may be mentioned:

(i) The standard conjugated paths (CPs) embracing two, three and four linearly-connected C=C bonds (CP(2)s, CP(3)s and CP(4)s) contribute significantly to terms of power series for total energies of the second, fourth and sixth orders, respectively;

(ii) The afore-mentioned contributions always are of positive signs (in negative energy units) and thereby of stabilizing nature;

(iii) Relative values of the contributions concerned depend upon total numbers of the respective standard CPs present in the given hydrocarbon. In particular, contributions of CP(2)s and CP(3)s to energy corrections of the second and fourth orders, respectively, are expressible as sums of transferable increments of individual CPs and thereby these are directly proportional to the numbers of the latter;
The decisive energy correction of the second order (coinciding with the Dewar energy of the PMO theory [14]) is determined exclusively by the number of the simplest conjugated paths (CP(2)s) embracing two C=C bonds connected by a C-C bond.

Again, application of the perturbative approach to relative stabilities of pi-electron systems of polyenes undertaken in the above study contributes to an extension of the very concept and/or model of conjugated paths. This conclusion is based on the following properties of the power series for total energies:

(i) Members of the series of the fourth ($E(4)$) and sixth orders ($E(6)$) contain both positive (stabilizing) and negative (destabilizing) components and these are in some relation one with another in addition. This implies that destabilizing factors also manifest themselves in polyenes that are able to play an equally decisive role in the formation of the final total energy;

(ii) Negative (destabilizing) components of the energy corrections $E(4)$ and $E(6)$ are interpretable as contributions of conjugated paths of a non-standard (composite) nature defined as successive products of two or three connected standard CP(2)s and/or CP(3)s. Moreover, the self-returning composite conjugated paths (SRCCPs) prove to be especially important, wherein an even number of C=C bonds is involved and each of them is visited twice;

(iii) The usual linear conjugated paths embracing four C=C bonds (CP(4)s) are not the only fragments (substructures) participating in the formation of positive (stabilizing) components of the sixth order energy. In particular, four-membered fragments containing both a linearly-conjugated segment and a cross-conjugated one [the so-called semi-conjugated paths (SCP(4)s)] also contribute to the sixth order stabilization of polyenes;

(iv) The energy correction of the sixth order generally is a non-additive quantity with respect to increments of individual participating fragments (substructures) including the standard CPs. Consequently, the total value of this correction depends upon the actual mutual arrangement of these fragments in the given hydrocarbon.

Consideration of specific examples also corroborates the extended nature and, consequently, a higher discriminative potential of the perturbative approach applied
vs. the usual CP model. In this respect, the most important conclusions are as follows:

(i) Destabilizing increments of self-returning composite conjugated paths (SRC-CPs) prove to be generally responsible for lower relative stabilities of branched isomers of polyenes vs. their linear counterparts;

(ii) Isomers of extended polyenes containing different numbers of semi-conjugated paths (SCPs) usually are represented by distinct sixth order energies even if the relevant numbers of the standard CPs are uniform.

Appendix

A Derivation of expressions for the sixth order energy corrections

In its most general form, the power series for total energies of molecules and molecular systems has been originally derived in Ref.[17]. This study contains members of the power series up to fourth order \((k = 4)\). The relevant fifth order terms may be found in Ref.[15]. A direct extension of the above-cited derivation to terms of higher orders (including the sixth order ones) is a rather cumbersome procedure. In this connection, we will confine ourselves here to a less general Hamiltonian matrix vs. that of Refs. [17,18] as described below. Nevertheless, the overall methodology to be invoked closely resembles the original one [17]. The main points of the latter are as follows: First, the interrelation [36] is employed between the total energy being sought \((\mathcal{E})\), the Hamiltonian matrix of the system(s) concerned \((\mathbf{H})\) and the relevant representation of the one-electron density matrix (the charge- bond order (CBO) matrix) \(\mathbf{P}\), viz.

\[
\mathcal{E} = Tr(\mathbf{PH}).
\]  

(A1)

Second, the matrix \(\mathbf{P}\) is derived directly [18] on the basis of solution of the so-called commutation equation [36]. For Hamiltonian matrices \((\mathbf{H})\) consisting of zero and first order members \((\mathbf{H}_0)\) and \((\mathbf{H}_1)\), respectively), the above-mentioned solution may be carried out perturbatively. As a result, both the CBO matrix \(\mathbf{P}\) and the total energy \(\mathcal{E}\) are expressible as sums of corrections \(\mathbf{P}_k\) and \(\mathcal{E}_k\) of increasing orders \(k\).
Moreover, each energy correction $\mathcal{E}(k)$ is additionally representable as a sum of two components, viz.

$$\mathcal{E}(k) = \mathcal{E}^{(\alpha)}(k) + \mathcal{E}^{(\beta)}(k), \quad \mathcal{E}^{(\alpha)}(k) = Tr(P(k)H(0)), \quad \mathcal{E}^{(\beta)}(k) = Tr(P(k-1)H(1)). \quad (A2)$$

The most general Hamiltonian matrix ($H$) underlying the original derivation of $\mathcal{E}(k)$ [17] is as follows

$$H = H(0) + H(1) = \begin{bmatrix} E_+ & 0 \\ 0 & -E_- \end{bmatrix} + \begin{bmatrix} S & R \\ R^+ & Q \end{bmatrix}, \quad (A3)$$

where $E_+, E_-, S, R$ and $Q$ are certain $N \times N$-dimensional submatrices. Systems underlying the matrix $H$ and details of its construction (see e.g.[15,17]) are of no importance here. Let us note only that the relevant $2N$-dimensional basis set $\{\Psi\}$ is assumed to consist of two well-separated $N$-dimensional subsets $\{\Psi_+(\cdot)\}$ and $\{\Psi_-(\cdot)\}$. The minus sign in front of $E_-$ of Eq.(A3) is introduced for convenience. The superscript $+$ designates the transposed (Hermitian-conjugate) matrix.

The above-exhibited form of the initial Hamiltonian matrix $H$ allowed us to look for the CBO matrix $P$, separate members of the power series of which ($P(k)$) also are divisible into four submatrices (blocks). Moreover, a new version of the Rayleigh-Schrödinger perturbation theory (RSPT) has been formulated, wherein entire submatrices (blocks) of the matrix $H$ (i.e. non-commutative quantities) play the central role instead of usual (commutative) matrix elements. Accordingly, the new PT [19,20] has been called non-commutative RSPT (NCRSPT). As a result of its application, the corrections $P(k)$ take the following form

$$P(k) = -2 \begin{bmatrix} X_+^{(k)} & G^{(k)} \\ G^+^{(k)} & -X_-^{(k)} \end{bmatrix}, \quad (A4)$$

where $G^{(k)}$ are the so-called principal matrices of the NCRSPT determined by certain matrix equations [18-20]. Meanwhile, diagonal positions of the corrections $P(k)$ are occupied by matrices $X_+^{(k)}$ and $X_-^{(k)}$ that have been referred to as intrasubset population matrices. These correspondingly refer to subsets $\{\Psi_+(\cdot)\}$ and $\{\Psi_-(\cdot)\}$ and are expressible in the form of sums of products of matrices $G^{(k)}$ of lower orders as exemplified below by Eqs. (A9) and (A15). The original derivation of members ($P(k)$) of power series for the matrix $P$ [18] embraced terms to within second order only. Nevertheless, it is easily extendable to any $k$. 
As already mentioned, we confine ourselves here to a particular case of the matrix \( \mathbf{H} \) of Eq.(A3). To this end, let us accept the equality \( \mathbf{E}(+) = \mathbf{E}(-) = \mathbf{I} \). [Besides, the resulting simplified Hamiltonian matrix coincides with that following from the initial matrix of our study shown in Eq.(1) after transforming the latter into the basis of bond orbitals (BOs) \( \{ \varphi \} \)[15]. (submatrices \( \mathbf{I} \) and \( -\mathbf{I} \) correspondingly represent one-electron energies of bonding BOs (BBOs) and of antibonding BOs (ABOs)]. The most important advantage of the above-specified condition consists in the possibility of an algebraic solution of matrix equations determining the principal matrices of the NCRSPT \( \mathbf{G}(k), k = 1, 2, 3,... \). As a result, these matrices meet the following recurrence relations

\[
\mathbf{G}(k) = -\frac{1}{2}(\mathbf{S}\mathbf{G}(k-1) - \mathbf{G}(k-1)\mathbf{Q}) - \mathbf{L}(k),
\]

where \( \mathbf{L}(k) \) are products of the same matrices of lower orders, e. g.

\[
\mathbf{L}(1) = \mathbf{L}(2) = 0, \quad \mathbf{L}(3) = 2\mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(1),
\]

\[
\mathbf{L}(4) = \mathbf{G}(2)\mathbf{G}^+(1)\mathbf{G}(1) + 2\mathbf{G}(1)\mathbf{G}^+(2)\mathbf{G}(1) + \mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(2), \text{ etc.}
\]

Finally, a useful relation \( \mathbf{R} = -2\mathbf{G}(1) \) follows for first order matrices in this case. Substituting the latter relation along with Eqs.(A3) and (A4) into Eq.(A2) yields the following expressions for separate components of the sixth order energy, viz.

\[
\mathcal{E}^{(\alpha)}(6) = -4\text{Tr}(\mathbf{X}(6)^+),
\]

\[
\mathcal{E}^{(\beta)}(6) = -2\text{Tr}(\mathbf{X}(5)^+\mathbf{S} - \mathbf{X}(5)^-\mathbf{Q}) + 8\text{Tr}(\mathbf{G}(5)\mathbf{G}(1)^+).
\]

Let us now consider the components of Eqs.(A7) and (A8) separately. The matrix \( \mathbf{X}(6)^+ \) determining the first component \( \mathcal{E}^{(\alpha)}(6) \) is expressible as follows

\[
\mathbf{X}(6)^+ = -\mathbf{G}(5)\mathbf{G}(1) + \mathbf{G}(1)\mathbf{G}(5) + \mathbf{G}(4)\mathbf{G}(2) + \mathbf{G}(2)\mathbf{G}(4) + \mathbf{G}(3)\mathbf{G}(3) + \\
+ 2\mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}^+(1) \mathbf{G}^+(1) + \mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(1)\mathbf{G}^+(1) \mathbf{G}^+(1) + \\
+ \mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(3)\mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1) + \mathbf{G}(3)\mathbf{G}^+(1)\mathbf{G}(1)\mathbf{G}^+(1) \mathbf{G}^+(1) + \\
+ \mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(2)\mathbf{G}^+(2) \mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1) + \mathbf{G}(1)\mathbf{G}^+(1)\mathbf{G}(2)\mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1) + \\
+ \mathbf{G}(2)\mathbf{G}^+(1)\mathbf{G}(1)\mathbf{G}^+(2) \mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1) + \mathbf{G}(2)\mathbf{G}^+(1)\mathbf{G}(2)\mathbf{G}^+(1) \mathbf{G}^+(1) \mathbf{G}^+(1). \quad (A9)
\]

Substituting the above formula into Eq.(A7) shows that the component \( \mathcal{E}^{(\alpha)}(6) \) contains matrices \( \mathbf{G}(k) \) up to \( k = 5 \). The next step then consists in eliminating the matrices
$G_{(5)}$ and $G_{(4)}$ from the expression concerned on the basis of our previous experience when dealing with similar relations. To this end, let us take $Tr(G_{(5)}G_{(1)}^+) \text{ and } Tr(G_{(4)}G_{(2)}^+)$ separately and substitute recurrence relations of Eq. (A5) for $G_{(5)}$ and $G_{(4)}$, respectively. Moreover, Eq. (A6) also should be used along with allowed cyclic transpositions of matrices inside the $Trace$ signs. The results of these procedures are as follows

$$Tr(G_{(5)}G_{(1)}^+) = Tr(G_{(3)}G_{(3)}^+) - 2Tr(G_{(3)}G_{(1)}^+ G_{(1)}^+) - 2Tr(G_{(1)}G_{(1)}^+ G_{(2)}G_{(2)}^+) - 2Tr(G_{(1)}G_{(2)}^+ G_{(1)}^+) - 2Tr(G_{(1)}^+ G_{(1)}^+ G_{(1)}G_{(1)}^+),$$  \hspace{1cm} (A10)$$

$$Tr(G_{(4)}G_{(2)}^+) = Tr(G_{(3)}G_{(3)}^+) - 2Tr(G_{(3)}G_{(1)}^+ G_{(1)}^+) - Tr(G_{(1)}G_{(1)}^+ G_{(2)}G_{(2)}^+) - 2Tr(G_{(1)}^+ G_{(1)}G_{(1)}^+ G_{(1)}^+),$$  \hspace{1cm} (A11)$$

Employment of Eqs. (A7) and (A9)-(A11) then yields the following formula for $E^{(\alpha)}_{(6)}$

$$E^{(\alpha)}_{(6)} = -20Tr(G_{(3)}G_{(3)}^+) - 16Tr(G_{(3)}G_{(1)}^+ G_{(1)}^+) + 16Tr(G_{(1)}G_{(1)}^+ G_{(2)}G_{(2)}^+) + 16Tr(G_{(1)}G_{(1)}^+ G_{(2)}G_{(2)}^+) + 8Tr(G_{(1)}^+ G_{(1)}G_{(1)}^+ G_{(1)}^+),$$  \hspace{1cm} (A12)$$

that, in turn, may be simplified considerably after eliminating $Tr(G_{(3)}G_{(1)}^+ G_{(1)}G_{(1)}^+)$.

To this end, the following relation should be used, viz.

$$Tr(G_{(3)}G_{(1)}^+ G_{(1)}G_{(1)}^+) = Tr(G_{(1)}G_{(1)}^+ G_{(2)}G_{(2)}^+) - 2Tr(G_{(1)}G_{(1)}^+ G_{(1)}G_{(1)}^+) + Tr(G_{(1)}^+ G_{(1)}G_{(1)}^+ G_{(1)}G_{(1)}^+).$$  \hspace{1cm} (A13)$$

Derivation of Eq. (A13) may be carried out analogously to those of Eqs. (A10) and (A11). The final expression for $E^{(\alpha)}_{(6)}$ is then as follows

$$E^{(\alpha)}_{(6)} = -20Tr(G_{(3)}G_{(3)}^+) + 40Tr(G_{(1)}G_{(2)}^+ G_{(1)}^+) + 40Tr(G_{(1)}^+ G_{(1)}G_{(1)}^+ G_{(1)}^+).$$  \hspace{1cm} (A14)$$

The second component of the sixth order energy $(E^{(\beta)}_{(6)})$ also may be reformulated similarly. The first step of the relevant procedure consists in substituting into Eq. (A8) the expressions for $X_{(5)+}$ and $X_{(5)-}$, viz.

$$X_{(5)+} = G_{(4)}^+ G_{(1)}^+ + G_{(3)}^+ G_{(2)}^+ + G_{(2)} G_{(3)}^+ + G_{(1)}^+ G_{(1)}^+ G_{(1)}^+ G_{(2)}^+ +$$
\[ G(1) G^+(1) G(2) G^+(2) + G(1) G^+(2) G(1) G^+(1) + G(2) G^+(1) G(1) G^+(1), \]  
(A15)

\[ X(5) = G^+(4) G(1) + G^+(1) G(4) + G^+(3) G(2) + G^+(2) G(3) + G^+(1) G(1) G^+(1) G(2) + G^+(1) G(2) G^+(1) G(1) + G^+(2) G(1) G^+(1) G(1). \]  
(A16)

Thereupon, relations of Eqs.(A10), (A11) and (A13) should be invoked to eliminate \( \text{Tr}(G(5) G^+(1)) \), \( \text{Tr}(G(4) G^+(2)) \) and \( \text{Tr}(G(3) G^+(1) G^+(1)) \), respectively. The result is as follows

\[ E^{(3)}(6) = 24 \text{Tr}(G(3) G^+(3)) - 48 \text{Tr}(G(1) G^+(2) G(1) G^+(2)) - 48 \text{Tr}(G(1) G^+(1) G(1) G^+(1) G(1) G^+(1)). \]  
(A17)

After summing up the two components of the sixth order energy shown in Eqs.(A14) and (A17) in accordance with Eq.(A2), we finally obtain

\[ E_{(6)} = 4 \text{Tr}(G(3) G^+(3)) - 8 \text{Tr}(G(1) G^+(2) G(1) G^+(2)) - 8 \text{Tr}(G(1) G^+(1) G(1) G^+(1) G(1) G^+(1)). \]  
(A18)

The expression of Eq.(18) seems to be the most compact form of the correction concerned. However, it is not the most convenient one for practical applications, especially for the attempts of finding relations between separate increments of the overall correction \( E_{(6)} \), on the one hand, and individual interorbital interactions, on the other hand. The main reason for that consists in the rather involved nature of the matrix \( G(3) \). Indeed, the relevant definition shown in Eqs.(A5) and (A6) embraces the product \( G(1) G^+(1) G(1) \) (along with the \( G(2) \)-containing term) that gives birth to increments like that of the last term of Eq.(A18). To be able to sum up these similar increments, let us define a new matrix \( G^0(3) \) coinciding with the \( G(2) \)-containing term of Eq.(A5) for \( k = 3 \) as shown by the first relation of Eq.(12). Accordingly, the matrix \( G(3) \) of Eq.(A18) may be replaced by \( G^0(3) - 2G(1) G^+(1) G(1) \). Thereupon, we may get rid of the newly-emerging term \( \text{Tr}(G^0(3) G^+(1) G(1) G^+(1)) \) by constructing a relation like that of Eq.(A13). The final formula for \( E_{(6)} \) is then as follows

\[ E_{(6)} = 4 \text{Tr}(G^0(3) G^0(3)) + 8 \text{Tr}(G(1) G^+(1) G(1) G^+(1) G(1) G^+(1)) - 16 \text{Tr}(G(1) G^+(1) G(1) G^+(2) G^+(2)) - 16 \text{Tr}(G^+(1) G(1) G^+(2) G(2)) + 8 \text{Tr}(G(1) G^+(2) G(1) G^+(2)). \]  
(A19)
Separate terms of the above expression are exhibited in Eqs. (8)–(11) and discussed nearby. It deserves adding here that third and fourth increments of Eq.(A19) prove to be uniform in the case of AHs owing to the skew-symmetric nature of matrices $G_{(1)}$ and $G_{(2)}$ [28]. After summing up these increments, a single destabilizing component of the sixth order energy ($E_{(6)}^{(-)}$) arises (see Eq.(10)).

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