

A simple rationale for lowered stabilities of branched and cross-conjugated polyenes

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Abstract The study is aimed at revealing the decisive factors for relative stabilities of acyclic π -electron systems of polyenes, the carbon backbones of which are of different type of branching. The systems are modeled as sets of N weakly interacting double (C=C) bonds. The relevant total π -electron energies are represented in the form of power series containing members of even orders with respect to the averaged resonance parameter of single (C–C) bonds. For distinct isomers of the same polyene, both zero-order energies and respective second-order corrections are shown to take uniform values. Relative stabilities of these isomers are then primarily determined by the fourth-order member of the series that, in turn, consists of two additive components of opposite signs, viz., of the stabilizing component expressible as a sum of transferable increments of individual triplets of linearly conjugated C=C bonds [i.e., of the three-membered conjugated paths (CPs)] and of the destabilizing component depending on overall adjacencies (connectivity) of C=C bonds. Lower stabilities of π -electron systems of branched and/or cross-conjugated polyenes vs. the linear ones then follow from comparative analyses of the relevant fourth-order energies, and this destabilization is shown to originate either from (a) a reduced number of CPs or from (b) higher adjacencies of C=C bonds in the former isomers. An actual interplay of both factors (c) also is rather common. The three cases (a)–(c) are illustrated by specific examples.

Graphical abstract



Keywords Alkenes · Isomers · Molecular modeling · Conjugation energies · Polyenes

Introduction

Numerous computational methods are available nowadays that allow us to calculate any molecular property almost as accurately as it is required (see e.g. [1]). Meanwhile, understanding of rules and laws governing these properties lags behind [2–4] the extensive development of computations. To achieve the latter end, simplified approaches and models of molecules should be invoked.

The present study addresses qualitative aspects of thermodynamic stability of polyenes and especially the dependence of this characteristic upon the extent and type of branching of the carbon backbone. Recent advances in synthesis of fully cross-conjugated polyenes (dendralenes) [5, 6] followed by experimental investigations of their intriguing properties [5, 7, 8] stimulate an interest into the above-specified topic. The evident importance of the structure/property relations themselves also is among the underlying motives. Finally, polyenes (including the branched ones) play the role of reference structures in the Hess–Schaad group additivity scheme [9, 10], as well as serve as archetypal systems

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for polyconjugated organic materials widely applied in optoelectronics [8, 11].

Higher stabilities of (poly)conjugated compounds as compared to appropriate reference structures (see e.g. [12, 13]) generally follow from experimental heats of formation (e.g. two ethene molecules serve as a reference system for 1,3-butadiene). Moreover, the relevant difference is usually entirely ascribed to formation of a more extended united π -electron system and it is known as conjugation energy (although corrections for protobranching and hyperconjugation have been recommended recently [14]). At the Hückel level, total π -electron energies are commonly used to evaluate the extents of conjugation in related compounds and/or to rationalize the distinctions (see e.g. [10]).

Two alternative perspectives on the very polyene chain deserve mention in this context that yield extreme Hückel-type models of the relevant π -electron system. The first one concentrates mostly on constitution of the carbon backbone as a whole. Resonance parameters are assumed here to take uniform values for all carbon–carbon bonds for simplicity. The resulting model of polyene then coincides with the molecular graph (see e.g. [15]), the vertices and edges of which represent atoms and bonds, respectively. The relevant studies of conjugation energies [4, 13, 16–20] are carried out mostly by means of the chemical graph theory [15]. In particular, analysis of the principal Kekulé valence structure of polyene in terms of conjugated paths (CPs) of various lengths (i.e., of linear fragments consisting of C=C and C–C bonds alternately) [4, 21] appears to be fruitful in this field. An additional invoking of the main concepts of the valence bond (VB) theory (such as the Dewar resonance structures) also yields important conclusions concerning conjugation [13].

Another perspective on the same polyene chain consists in consideration of the latter as a set of weakly interacting double (C=C) bonds, where the single (C–C) bonds play the role of the interaction. Resonance parameters are then accordingly assumed to take significantly alternating values over the chain and perturbative approaches (overviewed below) are consequently applied. Advantages of this (perturbational) perspective over the former (graph-theoretical) one are as follows: first, it is in line with the chemical way of thinking about an involved compound as consisting of quasi-transferable elementary fragments, as well as with the classical definition of conjugation as an interaction of unsaturated functional groups. Second, it is compatible with the observed bond length alternation [12, 13] peculiar to polyenes of any size. Finally, application of alternating resonance parameters yields a proper chain-length dependence of the relevant excitation energies [22]. With this in mind, the present study is based on a perturbative treatment of π -electron systems of polyenes. Nevertheless, some concepts of graph-theoretical origin

also are invoked, in particular that of CPs [4, 21]. Accordingly, a considerable attention is paid to comparison of predictions of both approaches.

Development of the perturbational perspective on polyenes apparently started together with that of the well-known simple PMO theory [23]. Later, more sophisticated approaches to analysis of π -electron energies of polyene-like systems have been suggested, e.g. those based on perturbative treatments of configuration interaction (CI) [24, 25] (besides, the second energy expansion was asserted to converge [25] even in the case of uniform resonance parameters). Since the authors of these studies ultimately abandon many-electron wave functions and turn to interacting atomic or bond orbitals (AOs or BOs) when looking for chemically illustrative pictures of conjugation (delocalization) effects, the methods concerned may be regarded (and referred to) as indirect ones. Again, a perturbative expansion for total energies of molecules directly via certain submatrices (blocks) of the initial one-electron Hamiltonian matrix (\mathbf{H}) has been suggested recently [26–28], where \mathbf{H} was represented in the basis of either AOs or BOs and no CI was invoked. The derivation of this series was based on two points, viz., (a) the known interrelation between the total energy being sought (E), the one-electron Hamiltonian matrix of the system concerned (\mathbf{H}) and the relevant charge-bond order matrix (\mathbf{P}) [$E = \text{Trace}(\mathbf{PH})$] and (b) the direct method of obtaining the matrix \mathbf{P} by means of solution of the so-called commutation equation [29]. Since submatrices (blocks) of the matrix \mathbf{H} are non-commutative quantities (as opposed to usual matrix elements), the new perturbation theory (PT) has been called the non-commutative Rayleigh–Schrödinger PT (NCRSPT) [30, 31]. Application of this power series allowed us to discriminate between stabilities of π -electron systems of very similar constitution [28] in contrast to the simple PMO theory [23].

Let us return to polyenes themselves. The reduced stabilities of fully cross-conjugated polyenes (dendralenes) vs. the respective linear isomers is a well-established fact [5, 7, 8, 12, 13, 16, 24]. The regular constitution of these chain-like systems allows the relevant π -electron energies to be expressed algebraically and analyzed in the general case without specifying the number of carbon atoms [13, 16, 17, 24]. As a result, destabilization of dendralenes vs. linear polyenes has been traced back to unfavorable conditions for the so-called indirect delocalization in the cross-conjugated chain caused by specific orbital phase properties [24]. Recently, the same phenomenon has been accounted for by lower numbers of the Dewar resonance structures [13].

Dendralenes, however, make only a small part of branched polyenes: the majority of the latter are of irregular constitution and contain both linear and cross-conjugated

triplets of C=C bonds. As to theoretical studies, only a few contributions are devoted to the effect of the branching itself on the efficiency of π -conjugation. In this respect, the most general conclusion follows from the chemical graph theory, namely that “thermodynamic stability of polyenes decreases with branching” [17]. More specifically, the linear isomer $\text{H}_2\text{C}=(\text{CH})_{n-2}=\text{CH}_2$ was shown to have a maximal π -electron energy among all acyclic polyenes C_nH_{n+2} , whereas the 1,1'-divinyl isomer $[(\text{H}_2\text{C}=\text{CH})_2\text{C}(\text{CH})_{n-6}=\text{CH}_2]$ proved to take the second place [18]. Besides, predictions of relative stabilities of distinct isomers were mostly under focus of these studies rather than qualitative accounting for the results obtained.

The main aim of the present contribution consists in application of the power series for total energies of Refs. [26–28] to corroborate the reduced stabilities of π -electron systems of branched polyenes, in general, and of fully cross-conjugated ones, in particular, and to give an insight into the nature of this destabilization. The paper consists of two parts: the next (theoretical) section contains an overview of the principal points of the approach to be applied regarding the particular case of polyenes. Thereupon, specific examples are studied. Details concerning practical application of the power series for total energies are given in the “Appendix”.

Theory

Qualitative models of π -electron systems (including the standard Hückel (HMO) theory [32]) usually are formulated in the basis of $2p_z$ AOs of carbon atoms. To construct an initial Hamiltonian matrix of polyenes, let us also start with this basis set.

Let a certain polyene contain N uniform double (C=C) bonds and thereby $2N$ carbon atoms. The respective π -electron system will be then represented by an $2N$ -dimensional basis set of $2p_z$ AOs of these atoms $\{\chi\}$. The AOs will be characterized by uniform Coulomb parameters (α) and the equality $\alpha = 0$ will be accepted. Further, let resonance parameters between pairs of AOs of chemically bound atoms only be taken into consideration. The basis set $\{\chi\}$ may be then divided into two N -dimensional subsets $\{\chi^*\}$ and $\{\chi^o\}$ so that pairs of orbitals belonging to chemical bonds (C=C or C–C) find themselves in different subsets. This implies the non-zero resonance parameters to take place in the off-diagonal (intersubset) blocks of our initial Hamiltonian matrix. Accordingly, zero submatrices stand in the diagonal (intra-subset) positions of the latter (as is peculiar to alternant hydrocarbons in general [32–34]). Finally, let us enumerate the AOs in such a way that orbitals belonging to the same C=C bond (say, to the i th one) acquire the coupled numbers i and $N + i$ as exemplified in Fig. 1. As a result, resonance

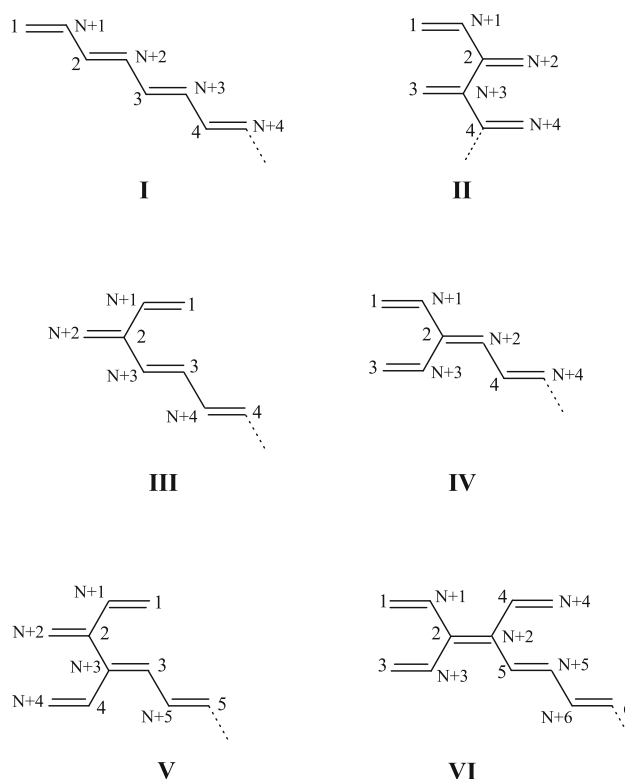


Fig. 1 Examples of polyenes of different types of branching, all of them containing N C=C bonds: the linear chain (I) and its fully cross-conjugated counterpart (II), as well as representatives of branched chains (III–VI). Numberings of carbon atoms and/or their $2p_z$ AOs also are shown, where AOs under numbers 1, 2, ..., N and $N + 1$, $N + 2$, ..., $2N$ belong to subsets $\{\chi^*\}$ and $\{\chi^o\}$, respectively

parameters of these strong bonds take the diagonal positions in the intersubset blocks of our matrix. Uniform values of these parameters (β) also are among natural assumptions here. Let our (negative) energy unit coincide with β in addition. The usual equality $\beta = 1$ then immediately follows. Similarly, the averaged resonance parameter of weak (C–C) bonds will be denoted by γ and supposed to be a sufficiently small (i.e., first order) term vs. the above-specified energy unit.

As a result, the initial Hamiltonian matrix of our polyene (\mathbf{H}) is representable as a sum of the zero-order member ($\mathbf{H}_{(0)}$) and of the first-order one ($\mathbf{H}_{(1)}$), including parameters of C=C and C–C bonds, respectively, viz.,

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} = \begin{vmatrix} \mathbf{0} & \mathbf{I} \\ \mathbf{I} & \mathbf{0} \end{vmatrix} + \begin{vmatrix} \mathbf{0} & \gamma\mathbf{B} \\ \gamma\mathbf{B}^+ & \mathbf{0} \end{vmatrix}, \quad (1)$$

where the orders are defined with respect to parameter γ and correspondingly denoted by subscripts (0) and (1). Notation \mathbf{I} here and below stands for the unit (sub)matrix and the superscript + designates the transposed (Hermitian-conjugate) matrix. Unit off-diagonal elements of the (sub)matrix \mathbf{B} (B_{ij} , $i \neq j$) correspond to C–C bonds, otherwise these take zero values. Meanwhile, the diagonal

elements vanish (i.e., $B_{ii} = 0$), because entire resonance parameters of C=C bonds are included into the zero-order matrix $\mathbf{H}_{(0)}$. Besides, no need arises here to specify the particular constitution of the given polyene. Thus, the matrix \mathbf{H} of Eq. (1) actually embraces the whole class of these hydrocarbons.

The above-introduced subsets of AOs $\{\chi^*\}$ and $\{\chi^o\}$ are characterized by a zero energy gap. Consequently, the perturbative approach of Refs. [26–28] cannot be straightforwardly applied to the matrix \mathbf{H} of Eq. (1) and a definite transformation of the basis set is required. To this end, let us turn to the basis of bond orbitals (BOs) of C=C bonds $\{\varphi\}$. The bonding BO (BBO) of the i th C=C bond and its antibonding counterpart (ABO) will be defined as a normalized sum and difference, respectively, of the relevant AOs χ_i^* and χ_{N+i}^o . These BOs will be correspondingly denoted by $\varphi_{(+)i}$ and $\varphi_{(-)i}$, where the subscript i refers to the i th bond. Finally, let us define the subset of BBOs $\{\varphi_{(+)}\}$ and that of ABOs $\{\varphi_{(-)}\}$. Passing from the initial basis $\{\chi\}$ to the new one $\{\varphi\}$ may be then represented by the following simple unitary matrix

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{I} & \mathbf{I} \\ \mathbf{I} & -\mathbf{I} \end{vmatrix}, \quad (2)$$

which serves to transform the initial matrix \mathbf{H} of Eq. (1). The new Hamiltonian matrix is as follows

$$\mathbf{H}' = \mathbf{H}'_{(0)} + \mathbf{H}'_{(1)} = \begin{vmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{vmatrix} + \begin{vmatrix} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^+ & \mathbf{Q} \end{vmatrix}, \quad (3)$$

where the superscript serves to distinguish between the present matrix and that of Eq. (1), and \mathbf{S} , \mathbf{Q} and \mathbf{R} are submatrices proportional to the above-specified parameter γ , viz.

$$\mathbf{S} = -\mathbf{Q} = \frac{\gamma}{2}(\mathbf{B} + \mathbf{B}^+), \quad \mathbf{R} = \frac{\gamma}{2}(\mathbf{B}^+ - \mathbf{B}). \quad (4)$$

Thus, the transformed Hamiltonian matrix (\mathbf{H}') also consists of a zero-order member ($\mathbf{H}'_{(0)}$) and of a first-order one ($\mathbf{H}'_{(1)}$) with respect to the same parameter γ , the former containing one-electron energies of BBOs and of ABOs in its diagonal positions (these correspondingly coincide with 1 and -1 in our energy units) and the latter embracing weak interactions between BOs of C=C bonds (interbond resonance parameters). Again, the $N \times N$ -dimensional submatrices of the matrix \mathbf{H}' refer to individual subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ and to their interaction. In particular, elements of submatrices \mathbf{S} , \mathbf{Q} , and \mathbf{R} of the first-order member $\mathbf{H}'_{(1)}$ represent the following types of the above-mentioned interactions

$$\begin{aligned} S_{ij} &= \langle \varphi_{(+)i} | \hat{H} | \varphi_{(+)j} \rangle, & Q_{lm} &= \langle \varphi_{(-)l} | \hat{H} | \varphi_{(-)m} \rangle, \\ R_{il} &= \langle \varphi_{(+)i} | \hat{H} | \varphi_{(-)l} \rangle, \end{aligned} \quad (5)$$

where the BOs concerned are shown inside the bra- and ket-vectors. Proportionality of these elements to γ seen from Eq. (4) reflects the fact that the interaction between C=C bonds takes place through C–C bonds. It is then no surprise that non-zero values of the elements concerned correspond only to pairs of BOs of C=C bonds connected by C–C bonds (and referred to below as the first-neighboring C=C bonds). Formally, the latter conclusion follows from Eq. (4) after taking into account the above-mentioned correspondence between non-zero elements of the (sub-)matrix \mathbf{B} and C–C bonds. Finally, the equality $B_{ii} = 0$ along with Eq. (4) yields zero values for intrabond resonance parameters S_{ii} , Q_{ii} and R_{ii} as exhibited below in Eq. (7).

The main good of the above-performed transformation is that the subsets $\{\varphi_{(+)}\}$ and $\{\varphi_{(-)}\}$ are now separated one from another by a substantial energy gap (equal to 2) vs. the intersubset interaction \mathbf{R} . Thus, the matrix \mathbf{H}' of Eq. (3) meets the requirements of the NCRSPT [30, 31] and thereby the perturbative approach of Refs. [26–28] may be applied. As a result, the total π -electron energy of polyenes (E) may be represented in the form of power series, i.e., as a sum of increments ($E_{(k)}$) of various orders k with respect to the averaged resonance parameter of C–C bonds (γ). The zero order member of this series ($E_{(0)}$) coincides with the total energy of N isolated C=C bonds ($2N$) in accordance with the expectation, whereas the first-order one ($E_{(1)}$) vanishes [26]. Meanwhile, each subsequent increment $E_{(k)}$ ($k > 1$) is expressible via products of the entire submatrices (blocks) \mathbf{S} , \mathbf{Q} , and \mathbf{R} and consequently contains the respective (k th) power (γ^k) of our parameter γ . The overall convergence of this series has been studied in Ref. [35]. Finally, analysis of formulae for $E_{(k)}$ [28] showed that non-zero corrections of odd orders ($k = 3, 5, \dots$) arise for (poly)cyclic systems only. That is why we will confine ourselves here to the most important corrections of even orders $E_{(2)}$ and $E_{(4)}$.

Before passing to these corrections, let us introduce the following principal matrices [26, 31, 36]

$$\begin{aligned} \mathbf{G}_{(1)} &= -\frac{1}{2}\mathbf{R}, \\ \mathbf{G}_{(2)} &= -\frac{1}{2}(\mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q}) = \frac{1}{4}(\mathbf{S}\mathbf{R} - \mathbf{R}\mathbf{Q}) \\ &= \frac{1}{4}(\mathbf{S}\mathbf{R} + \mathbf{R}\mathbf{S}), \end{aligned} \quad (6)$$

where the last relation is based on the equality $\mathbf{Q} = -\mathbf{S}$ seen from Eq. (4). Substituting Eq. (4) in Eq. (6) shows in addition that matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ correspondingly contain factors γ and γ^2 and thereby are of the first and second orders as indicated by the subscripts (1) and (2). Zero diagonal elements of the same matrices easily follow

from their skew-Hermitian nature [35]. The overall result concerning diagonal elements of our matrices takes then the form

$$S_{ii} = Q_{ii} = R_{ii} = G_{(1)ii} = G_{(2)ii} = 0. \quad (7)$$

Employment of matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ allows the energy corrections $E_{(2)}$ and $E_{(4)}$ to be represented in a compact and chemically illustrative form. Thus, the second-order member ($E_{(2)}$) takes a rather simple form, viz.

$$E_{(2)} = 4\text{Tr}(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+) > 0, \quad (8)$$

whereas the fourth-order one ($E_{(4)}$) consists of a sum of two components [27] defined as follows

$$\begin{aligned} E_{(4)}^{(+)} &= 4\text{Tr}(\mathbf{G}_{(2)}\mathbf{G}_{(2)}^+) > 0, \\ E_{(4)}^{(-)} &= -4\text{Tr}(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+) < 0. \end{aligned} \quad (9)$$

The notation Tr here and below stands for a trace of the whole matrix product within parentheses. The second and fourth orders of these corrections with respect to parameter γ may be easily verified using Eqs. (4), (6), (8), and (9). As is seen from Eqs. (8) and (9), traces of positive-definite matrices [37] of the type \mathbf{AA}^+ stand in these relations. This implies an a priori positive sign and thereby the stabilizing nature of the second-order energy $E_{(2)}$ (the negative energy unit should be recalled here). Meanwhile, the components of the fourth-order correction $E_{(4)}$ are of opposite signs as indicated by additional superscripts (+) and (-). From Eq. (7) it follows also that both the second-order energy $E_{(2)}$ and the positive component of the fourth-order one ($E_{(4)}^{(+)}$) contain no intrabond contributions. By contrast, the matrix product $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ determining the negative component of the fourth-order energy ($E_{(4)}^{(-)}$) is a symmetric (Hermitian) matrix. Consequently, diagonal elements $(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{ii}$ take non-zero values and prove to be responsible for a large part of this energy component [27].

Let us turn now to interpretation of the above-exhibited expressions. As is seen from Eqs. (5) and (6), the element $G_{(1)il}$ of the first-order matrix $\mathbf{G}_{(1)}$ connects the BBO $\varphi_{(+)i}$ and the ABO $\varphi_{(-)l}$. Moreover, it is proportional to the relevant interbond resonance parameter (R_{il}) and inversely proportional to the energy gap between BBOs and ABOs (equal to 2). The relevant implications are then as follows: first, the element $G_{(1)il}$ represents the direct (through-space) interaction between BOs $\varphi_{(+)i}$ and $\varphi_{(-)l}$. Second, non-zero values of these elements [i.e., of $G_{(1)il}$ and of $G_{(1)li}$] refer to BOs belonging to first-neighboring C=C bonds as it was the case with resonance parameters R_{il} and R_{li} . In other words, two significant elements of the matrix $\mathbf{G}_{(1)}$ correspond to any C-C bond and/or to any butadiene-like fragment of the given polyene [vanishing direct intrabond interactions $G_{(1)ii}$ also are taken into consideration here (see Eq. 7)]. If we

invoke now the concept of the simplest conjugated path [4, 21] embracing two C=C bonds and abbreviated below as CP(2), an analogous two-to-one correspondence follows immediately between significant direct interbond interactions and CP(2)s. Accordingly, the total number of non-zero elements of the matrix $\mathbf{G}_{(1)}$ coincides with the twofold number of these paths in the given polyene. Finally, the above-specified significant elements are local in their nature and, consequently, take uniform values for all CP(2)s. These simple rules are illustrated by specific examples in the next section [see e.g. Eq. (11)].

Let us recall now that the matrix $\mathbf{G}_{(1)}$ gives birth to the positive (stabilizing) second-order energy of Eq. (8). All CP(2)s of our polyene then contribute uniform increments to this energy and the latter is consequently proportional to the number of these paths. This, in turn, implies coinciding second-order energies for distinct isomers of the same polyene, usually containing uniform numbers of C-C bonds and thereby of CP(2)s (see also the next section). It is evident that fourth-order energies start to play the decisive role in this case. Thus, let us now turn to second-order matrices $\mathbf{G}_{(2)}$ and $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ underlying these important increments.

Elements ($G_{(2)il}$) of the matrix $\mathbf{G}_{(2)}$ are interpretable as indirect (through-bond) interactions of the same BOs ($\varphi_{(+)i}$ and $\varphi_{(-)l}$). Indeed, from Eq. (6) we obtain

$$G_{(2)il} = \frac{1}{4} \left[\sum_{(+j)} S_{ij}R_{jl} - \sum_{(-m)} R_{im}Q_{ml} \right], \quad (10)$$

where sums over (+)j and over (-)m correspondingly embrace BBOs and 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 the $j \neq i$ and $m \neq l$ because of Eq. (7)]. Since the matrix $\mathbf{G}_{(2)}$ determines the positive (stabilizing) component of the fourth-order energy as Eq. (9) indicates, the interbond interactions concerned may be referred to as stabilizing indirect interactions. Similarly, the element $(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{ij}$ of the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ represents the indirect interaction between two BBOs ($\varphi_{(+)i}$ and $\varphi_{(+)j}$) via ABOs of the remaining C=C bonds ($\varphi_{(-)m}$). Accordingly, the diagonal element $(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{ii}$ may be interpreted as the indirect self-interaction of the BBO $\varphi_{(+)i}$ via ABOs. As these elements contribute to the destabilizing component of the fourth-order energy [see Eq. (9)], we will call them destabilizing indirect interactions.

Therefore, an additional stabilization (or destabilization) of the π -electron system of a certain polyene vs. the relevant second-order energy depends upon the outcome of an interplay between the above-specified two types of indirect interactions of BOs. That is why the interrelation becomes of importance between relative efficiencies of these interactions and constitution of the given hydrocarbon. To

clarify this point, let us dwell now on conditions that ensure significant values of the relevant matrix elements.

In the case of elements $G_{(2)il}$ defined by Eq. (10), the orbitals $\varphi_{(+j)}$ and $\varphi_{(-m)}$ should overlap directly both with $\varphi_{(+i)}$ and with $\varphi_{(-l)}$ to be efficient mediators. Hence, non-zero values of the stabilizing indirect interactions may correspond only to pairs of second-neighboring C=C bonds possessing a common first neighbor. As opposed to the first-order elements $G_{(1)il}$, however, presence of such a neighbor (say, of the M th C=C bond in between the I th and the L th one) is not sufficient for a significant element $G_{(2)il}$ to arise: 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, 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 two increments cancel out one another for the cross-conjugated arrangement of bonds I, M, and L and the relevant element vanishes (see the “Appendix” for details). In summary, two non-zero elements ($G_{(2)il}$ and $G_{(2)li}$) correspond to BOs of the terminal bonds I and L of any linear hexatriene-like fragment I–M–L and thereby to any CP embracing three C=C bonds and abbreviated below as CP(3) [the remaining elements $G_{(2)ii}$, $G_{(2)im}$ and $G_{(2)ml}$ vanish because of Eq. (7)]. Accordingly, the total number of non-zero elements of a certain matrix $G_{(2)}$ coincides with the twofold number of CP(3)s in the relevant system. Uniform absolute values of these significant elements also easily follow from the definition of Eq. (10). Consequently, the stabilizing component $E_{(4)}^{(+)}$ of the fourth-order energy $E_{(4)}$ consists of a sum of transferable increments of individual CP(3)s and thereby it is determined by the total number of these paths.

Further, an element $(G_{(1)}G_{(1)}^+)_{ij}$ does not vanish, if in the given system there is an ABO $\varphi_{(-m)}$ such that both $G_{(1)im}$ and $G_{(1)jm}$ ($G_{(1)mj}^+$) take non-zero values. 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 $\varphi_{(-m)}$ necessarily belongs to a third (M th) C=C bond, where $M \neq I$ and $M \neq J$. Again, the bonds under numbers I and M, as well as M and J should be first neighboring to ensure non-zero elements $G_{(1)im}$ ($G_{(1)mi}$) and $G_{(1)jm}$ ($G_{(1)mj}$) as discussed above. Thus, an off-diagonal element $(G_{(1)}G_{(1)}^+)_{ij}$ ($i \neq j$) takes a non-zero value for any pair of second-neighboring C=C bonds I and J possessing a common first neighbor M (the mutual arrangement of the three bonds plays no role here). This implies that the higher is the total number of the second-neighboring pairs of C=C bonds in the given polyene, the more significant is the destabilizing component of the fourth-order energy. Furthermore, a diagonal element $(G_{(1)}G_{(1)}^+)_{ii}$ (also contributing to $E_{(4)}^{(-)}$ [27]) is proportional to the number of first neighbors of the respective (i.e., of the I th) C=C

bond. The total absolute value of the negative (destabilizing) energy component $E_{(4)}^{(-)}$ may be then concluded to be determined by overall adjacencies (connectivity) of C=C bonds in the given polyene. As a result, an extra destabilization of more compact isomers vs. the less compact ones is anticipated.

It is seen, therefore, that differences in total fourth-order energies of isomers of a certain polyene (if any) may originate either (a) from distinct numbers of CP(3)s or (b) from dissimilar adjacencies of C=C bonds. Manifestation of both factors simultaneously (c) also cannot be excluded. These cases are exemplified in the next section.

Results and discussion

Let us start with the linear polyene (I) and its fully cross-conjugated isomer (dendralene) (II), both of them containing the same number of C=C bonds N (Fig. 1). The relevant zero-order energies also are uniform [$E_{(0)}(I) = E_{(0)}(II) = 2N$] along with the numbers of C–C bonds ($N - 1$) and thereby of CP(2)s. In respect of CPs of higher orders, however, the systems I and II differ from one another substantially, e.g. these contain $N - 2$ and zero CP(3)s, respectively.

The principal first-order matrices ($G_{(1)}$) representing the linear polyenes (I) were shown to take a common form valid for any N [28]. The same may be easily demonstrated for dendralenes (II) as well. Let $G_{(1)}(I)$ and $G_{(1)}(II)$ stand for these unified matrices. We then obtain

$$G_{(1)}(I) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & 0 & 0 & \dots \\ -1 & 0 & 1 & 0 & \dots \\ 0 & -1 & 0 & 1 & \dots \\ 0 & 0 & -1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix}, \quad (11)$$

$$G_{(1)}(II) = -\frac{\gamma}{4} \begin{vmatrix} 0 & 1 & 0 & 0 & \dots \\ -1 & 0 & -1 & 0 & \dots \\ 0 & 1 & 0 & 1 & \dots \\ 0 & 0 & -1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix},$$

where a γ -dependent factor ($-\gamma/4$) is introduced in front of matrices concerned for convenience (construction of these matrices is exemplified in the “Appendix”). It is seen that two non-zero elements (e.g. $G_{(1)12}$ and $G_{(1)21}$, $G_{(1)23}$ and $G_{(1)32}$, etc.) correspond to any pair of first-neighboring C=C bonds ($C_1 = C_{N+1}$ and $C_2 = C_{N+2}$, $C_2 = C_{N+2}$ and $C_3 = C_{N+3}$, etc.) in the above-exhibited matrices and thereby to any CP(2) of our polyenes. These significant elements take uniform absolute values in addition. Thus, constitutions of matrices $G_{(1)}(I)$ and $G_{(1)}(II)$ are in line with expectations of the above section. Furthermore, matrices of Eq. (11) resemble one another except for signs of some elements. As a result, the

second-order energies $E_{(2)}(I)$ and $E_{(2)}(II)$ also are uniform and proportional to the respective number of CP(2)s ($N - 1$), viz., these coincide with $\gamma^2(N - 1)/2$.

Similarly, the matrix products $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+$ representing the chains I and II also differ one from another only in signs of their off-diagonal elements in accordance with the same adjacencies of C=C bonds in the polyenes concerned. Indeed, the terminal and the internal C=C bonds possess one and two first neighbors, respectively, in both chains. Consequently, diagonal elements of both matrices $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(I)$ and $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(II)$ coincide with 1,2,2...2,1 (note that $\gamma^2/16$ stands for the front factor in this case). Moreover, non-zero off-diagonal elements (equal either to 1 or to -1) occupy the second-neighboring positions $[(i, i + 2)$ and $(i - 2, i)]$ in the same matrix products, the total number of these elements coinciding with $2(N - 2)$, i.e., with the twofold number of second-neighboring pairs of C=C bonds in the chains I and II [matrices of Eq. (18) serve here as examples]. As a result, the relevant destabilizing components of the fourth-order energies also are uniform, viz.

$$\begin{aligned} E_{(4)}^{(-)}(I) &= E_{(4)}^{(-)}(II) = -\frac{\gamma^4}{64} \{ [4(N - 2) + 2] + [2(N - 2)] \} \\ &= -\frac{\gamma^4}{32} (3N - 5), \end{aligned} \quad (12)$$

where the contributions of diagonal and of off-diagonal elements are shown within first and second square brackets, respectively.

Let us turn now to the remaining second-order matrices $\mathbf{G}_{(2)}(I)$ and $\mathbf{G}_{(2)}(II)$ along with consequent stabilizing fourth-order energy components. For the linear isomer I, Eqs. (6), (9), and (11) yield the following formulae

$$\begin{aligned} \mathbf{G}_{(2)}(I) &= \frac{\gamma^2}{8} \begin{vmatrix} 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & \dots \\ -1 & 0 & 0 & 0 & \dots \\ 0 & -1 & 0 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix}, \\ E_{(4)}^{(+)}(I) &= \frac{4\gamma^4(N - 2)}{32}, \end{aligned} \quad (13)$$

where $\gamma^2/8$ is used now as a front factor. The expression for $\mathbf{G}_{(2)}(I)$ of Eq. (13) illustrates the above-concluded two-to-one correspondence between non-zero elements of the matrix $\mathbf{G}_{(2)}$ and individual CP(3)s. Proportionality between $E_{(4)}^{(+)}(I)$ and the number of these paths ($N - 2$) also is seen. The fact that both $\mathbf{G}_{(2)}(I)$ and $E_{(4)}^{(+)}(I)$ vanish for the CP(3)-free butadiene ($N = 2$) causes no surprise here. The total fourth-order energy of the chain I ($E_{(4)}(I)$) is shown in Table 1 and proves to be proportional to $N - 3$. Thus, the correction $E_{(4)}(I)$ is a positive quantity for $N > 3$ owing to predominance of its stabilizing component $E_{(4)}^{(+)}(I)$ over the destabilizing one $E_{(4)}^{(-)}(I)$. This implies the sufficiently long

Table 1 Stabilizing ($E_{(4)}^{(+)}$) and destabilizing ($E_{(4)}^{(-)}$) fourth-order energy components for isomers I–VI along with the relevant total values ($E_{(4)}$)

Isomer	CP(3)s	$E_{(4)}^{(+)}$	$E_{(4)}^{(-)}$	$E_{(4)}$	$E_{(4)}(N = 10)$
I	$N - 2$	$\frac{4\gamma^4(N - 2)}{32}$	$-\frac{\gamma^4(3N - 5)}{32}$	$\frac{\gamma^4(N - 3)}{32}$	$\frac{7\gamma^4}{32}$
II	0	0	$-\frac{\gamma^4(3N - 5)}{32}$	$-\frac{\gamma^4(3N - 5)}{32}$	$-\frac{25\gamma^4}{32}$
III	$N - 3$	$\frac{4\gamma^4(N - 3)}{32}$	$-\frac{\gamma^4(3N - 5)}{32}$	$\frac{\gamma^4(N - 7)}{32}$	$\frac{3\gamma^4}{32}$
IV	$N - 2$	$\frac{4\gamma^4(N - 2)}{32}$	$-\frac{3\gamma^4(N - 1)}{32}$	$\frac{\gamma^4(N - 5)}{32}$	$\frac{5\gamma^4}{32}$
V	$N - 3$	$\frac{4\gamma^4(N - 3)}{32}$	$-\frac{3\gamma^4(N - 1)}{32}$	$\frac{\gamma^4(N - 9)}{32}$	$\frac{\gamma^4}{32}$
VI	$N - 1$	$\frac{4\gamma^4(N - 1)}{32}$	$-\frac{\gamma^4(3N + 1)}{32}$	$\frac{\gamma^4(N - 5)}{32}$	$\frac{5\gamma^4}{32}$

The respective numbers of CP(3)s and an example of $E_{(4)}$ for the case $N = 10$ are shown in the second and the last columns, respectively

linear polyenes to be additionally stabilized vs. the sum $E_{(0)}(I) + E_{(2)}(I)$ due to the fourth-order energy. By contrast, the alternating signs of elements when passing from one line of the matrix $\mathbf{G}_{(1)}(II)$ of Eq. (11) to another gives birth to a zero matrix $\mathbf{G}_{(2)}(II)$ for dendralenes in accordance with absence of CP(3)s in these chains. As a result, the stabilizing fourth-order energy component $E_{(4)}^{(+)}(II)$ vanishes. The total correction $E_{(4)}(II)$ then coincides with $E_{(4)}^{(-)}(II)$ of Eq. (12) and takes a negative value for any N .

Therefore, the above results support lower relative stabilities of π -electron systems of dendralenes [5, 7, 8, 12, 13, 16, 24] as compared to those of linear polyenes. Moreover, the destabilization concerned is unambiguously traced back to the absence of CP(3)s in the cross-conjugated chain in contrast to the linear one. An analogous conclusion easily follows also from the simple CP model [4, 21]. In contrast to the latter, however, an additional destabilizing factor is now revealed to manifest itself in both systems under comparison that is related to connectivity (adjacencies) of C=C bonds. Only because of the above-established coincidence of the relevant energy increments $E_{(4)}^{(-)}(I)$ and $E_{(4)}^{(-)}(II)$, the destabilizing factor becomes irrelevant when comparing relative stabilities of linear and cross-conjugated polyenes. Besides, an alternative viewpoint to the same results also is possible: destabilization of a certain dendralene (II) vs. the linear isomer (I) [coinciding with $E_{(4)}^{(+)}(I)$ of Eq. (13)] is proportional to the number ($N - 2$) of cross-conjugated triplets of C=C bonds and/or of branching sites, each of them contributing $4\gamma^4/32$. An analogous proportionality followed also from the chemical graph theory [17].

Let us turn now to isomers of less regular constitution also containing N C=C bonds. Let us start with a single-branched chain III (Fig. 1), consisting of the main linear $N - 1$ -membered subchain and of a vinyl group ($C_1 = C_{N+1}$) attached to the second carbon atom of the former. It is evident that the system III contains $N - 1$ C=C bonds and thereby $N - 1$ CP(2)s as previously. Thus, both the zero-order energy of this new system and the relevant second-order correction coincide with

the former values for I and II. Moreover, an analogous coincidence (seen from Table 1) may be easily proven for destabilizing components of the fourth-order energies. This result causes little surprise if we bear in mind the same adjacencies of C=C bonds in the chains I, II, and III. Meanwhile, the number of CP(3)s is lower in the single-branched chain III and coincides with $N-3$. This implies a reduced number of non-zero elements in the matrix $\mathbf{G}_{(2)}(III)$ as compared to $\mathbf{G}_{(2)}(I)$ of Eq. (13) (the BOs of bonds $C_1 = C_{N+1}$ and $C_3 = C_{N+3}$ are characterized by zero elements $G_{(2)13}$ and $G_{(2)31}$ in the chain III in contrast to I). As a result, the relevant stabilizing component $E_{(4)}^{(+)}(III)$ is proportional to $N-3$ and proves to be reduced by $4\gamma^4/32$ as compared to $E_{(4)}^{(+)}(I)$ of Eq. (13). Finally, the total fourth-order correction $E_{(4)}(III)$ contains a factor $N-7$ and also is lowered analogously vs. $E_{(4)}(I)$.

Thus, the single-branched isomer III is predicted to be destabilized vs. the linear one (I) for the same reason, i.e., due to the reduced number of CP(3)s. The relevant extent of destabilization now equals to $4\gamma^4/32$ and coincides with the above-discussed increment of a single triplet of cross-conjugated C=C bonds.

Let us now consider another example (IV) of single-branched chains, where the vinyl group is “shifted” from the second carbon atom of the main subchain to the third one. This system (Fig. 1) also contains N C=C and $N-1$ C–C bonds. Thus, let us turn immediately to the relevant second-order matrices and fourth-order energies.

The matrix $\mathbf{G}_{(2)}(IV)$ involves $2(N-2)$ non-zero off-diagonal elements as it was the case with the matrix $\mathbf{G}_{(2)}(I)$ of Eq. (13). This result is not surprising if we bear in mind coinciding numbers of CP(3)s in the chains IV and I. Consequently, the relevant stabilizing components of fourth-order energies $E_{(4)}^{(+)}(IV)$ and $E_{(4)}^{(+)}(I)$ also are uniform and proportional to $N-2$. Meanwhile, matrices $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(IV)$ and $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(I)$ differ one from another significantly: first, the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(IV)$ contains elements 1,3,1,2,2,...,2,1 in its principal diagonal instead of 1,2,2,...,2,1 of the above-considered matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(I)$. This fact reflects distinct numbers of first neighbors for bonds $C_2 = C_{N+2}$ and $C_3 = C_{N+3}$ in the chains concerned. Second, the total number of non-zero off-diagonal elements is higher in the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(IV)$ as compared to $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(I)$ because of the growing number of second-neighboring pairs of C=C bonds when passing from I to IV. As a result, the sum of squares of all elements of the matrix $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(IV)$ exceeds that of $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(I)$. The destabilizing component of the fourth-order energy of the chain IV is then as follows

$$\begin{aligned} E_{(4)}^{(-)}(IV) &= -\frac{\gamma^4}{64} \{ [4(N-4) + 9 + 3] + [2(N-1)] \} \\ &= -\frac{3\gamma^4}{32} (N-1), \end{aligned} \quad (14)$$

and its absolute value is increased by $2\gamma^4/32$ as compared to that of Eq. (12) (the square brackets correspondingly contain contributions of diagonal elements and of off-diagonal ones as previously). As a result, the total correction $E_{(4)}(IV)$ is proportional to $N-5$. Hence, the relative stability of the system IV also is lower as compared to the linear isomer I. The underlying reason of this destabilization, however, proves to be entirely different from the above-established one and coincides now with growing connectivity (adjacencies) of C=C bonds when passing from I to IV.

Let us turn finally to double-branched polyene chains containing two triplets of cross-conjugated C=C bonds. The total number of these bonds coincides with N as previously.

Let us start with the system V (Fig. 1) and note immediately an evident analogy between the couple V and III, on the one hand, and that of IV and I, on the other hand. Implications of this analogy are as follows: first, the numbers of CP(3)s are uniform inside both couples of polyenes (these are correspondingly equal to $N-3$ and $N-2$). Second, adjacencies of C=C bonds grow when passing from III to V, as it was the case with I and IV. The same relations reveal themselves also when comparing the relevant fourth-order energy components. Thus, we obtain that $E_{(4)}^{(+)}(V)$ coincides with $E_{(4)}^{(+)}(III)$, both of them being proportional to $N-3$ (see Table 1). Meanwhile, the absolute value of $E_{(4)}^{(-)}(V)$ exceeds that of $E_{(4)}^{(-)}(III)$ by $2\gamma^4/32$ (the same distinction followed also from comparison of $E_{(4)}^{(-)}(IV)$ to $E_{(4)}^{(-)}(I)$). The total fourth-order energy $E_{(4)}(V)$ is then proportional to $N-9$. Hence, the double-branched chain V is destabilized by $2\gamma^4/32$ relatively to its single-branched counterpart III in accordance with the expectation. As with the above-considered passing from I to IV, the present destabilization also may be accounted for by growing adjacencies of C=C bonds. If we compare the double-branched chain V to the linear polyene I in addition, the overall destabilization of the former equals to $6\gamma^4/32$ and proves to be due to both factors, viz., to lowering of the number of CP(3)s and to the increasing adjacencies of C=C bonds.

Another (and the last) example (VI) contains two vinyl groups ($C_3 = C_{N+3}$ and $C_4 = C_{N+4}$) attached to the third and fourth carbon atoms of the main $N-2$ -membered subchain. Among examples of Fig. 1, this particular system contains the highest number of CP(3)s, namely $N-1$. The consequent fourth-order stabilizing energy component also accordingly takes a maximal value. An enhanced stability of the chain VI expected from the increased number of CP(3)s, however, is partially cancelled by the growing destabilizing component of the same energy equal to

$$\begin{aligned}
 E_{(4)}^{(-)}(VI) &= -\frac{\gamma^4}{64} \{[4(N-5) + 16 + 4] + [2(N+1)]\} \\
 &= -\frac{\gamma^4}{32} (3N+1)
 \end{aligned}
 \quad (15).$$

Comparison of this expression to the above ones indicates the component $E_{(4)}^{(-)}(VI)$ to be of the highest absolute value too. This result may be traced back to much higher adjacencies of C=C bonds in the most compact polyene VI. Indeed, the bond $C_2 = C_{N+2}$ possesses four first neighbors here and this fact is accompanied by an exclusively high matrix element $(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{22}$. Moreover, the number of second-neighboring pairs of C=C bonds now equals to $N+1$. The total fourth-order energy of our double-branched polyene VI is then ultimately proportional to $N-5$. As is seen from Table 1, the corrections $E_{(4)}(IV)$ and $E_{(4)}(VI)$ take the same value in spite of distinct particular components due to both different numbers of CP(3)s and dissimilar adjacencies of C=C bonds. This implies that π -electron systems of isomers under comparison are isoenergetic to within fourth-order terms inclusive. Thus, members of the sixth order of the same power series [38] should be invoked to discriminate them.

The whole set of fourth-order energies ($E_{(4)}$) shown in Table 1 (it is additionally exemplified by the particular case $N=10$) yields the following order of relative stabilities of π -electron systems of the above-studied isomers: $I > IV, VI > III > V > II$. Thus, the linear isomer (I) and the cross-conjugated one (II) are of the highest and lowest stabilities, respectively, whereas the remaining isomers (III–VI) take intermediate places.

Conclusions

Application of the power series for total energies of molecules [26–28] to π -electron systems of polyenes (undertaken in the present study) provides us with an efficient tool for qualitative evaluations and predictions of relative stabilities of isomers of different extent of branching, as well as for rationalization of their distinct stabilities (if any).

The fourth-order member of the series is shown to play the decisive role in the formation of the total π -electron energies of polyenes. This member, in turn, consists of a sum of two components of opposite signs. As a result, the actual stability of a certain π -electron system proves to be generally determined by the outcome of an interplay between two factors of opposite nature, viz., (a) of the stabilizing influence of linear conjugated fragments containing three C=C and two C–C bonds alternately (CP(3)s) and (b) of destabilization proportional to the overall

connectivity (adjacencies) of C=C bonds. If we recall here that the first factor only is taken into consideration in the simple CP model(s) [4, 21], the above-mentioned principal conclusion of the present study may be regarded as an extension of the important concept of conjugated paths.

The above-obtained results corroborate lower stabilities of fully cross-conjugated π -electron system of dendralenes (II) vs. the linear ones of usual polyenes (I) and indicate this phenomenon to be entirely due to the absence of CP(3)s in the former case. An analogous conclusion easily follows also from the qualitative CP model(s). The present analysis yields an accounting for such a success of this simple model: The reason is that the increments related to connectivity of C=C bonds are uniform owing to the same adjacencies of these bonds in the chains under comparison. Destabilization of π -electron systems due to reduced numbers of CP(3)s is found also for some partially cross-conjugated polyenes [e.g., for III (Fig. 1)], the adjacencies of C=C bonds of which coincide with those of I and/or II.

The above-concluded generalized nature of the approach applied vs. the CP model(s) becomes especially evident when passing to more compact branched isomers of polyenes, wherein C=C bonds possessing three and/or four neighbors also are present (e.g., the last three examples of Fig. 1). The point is that adjacencies (connectivity) of C=C bonds generally are higher in these systems and, consequently, the second (destabilizing) factor starts to play an equally important (or even a decisive) role in the formation of the actual stabilities of the relevant π -electron systems. As a result, some compact isomers of polyenes are predicted to be destabilized (vs. the linear chain I or another reference structure) even if the systems under comparison contain the same number of CP(3)s. In particular, the first representatives are expected to be less stable vs. the second ones in such couples of polyenes as IV and I, as well as V and III (Fig. 1) in spite of uniform numbers of CP(3)s equal to $N-2$ and $N-3$, respectively.

Appendix: Construction of the principal matrices. An example of hexatriene

Application of the above-suggested approach to a certain polyene consists of the following steps: first, we enumerate the initial AOs $\{\chi\}$ in the above-described manner. Second, we construct the relevant matrix \mathbf{B} and derive matrices $\mathbf{S}(-\mathbf{Q})$ and \mathbf{R} using Eq. (4). Finally, we find matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ on the basis of Eq. (6) and substitute them into expressions for energy corrections of Eqs. (8) and (9). To illustrate the construction of the above-enumerated principal matrices, let us dwell on the linear (VII) and branched (VIII) isomers of hexatriene (Fig. 2), coinciding with particular cases of chains I and II for $N=3$. The relevant

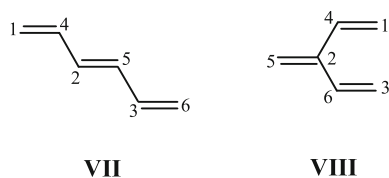


Fig. 2 The linear (VII) and branched (VIII) isomers of hexatriene. Numberings of $2p_z$ AOs of carbon atoms also are shown, where AOs under numbers 1, 2, 3 and 4, 5, 6 belong to subsets $\{\chi^*\}$ and $\{\chi^o\}$, respectively

initial matrices $\mathbf{B}(VII)$ and $\mathbf{B}(VIII)$ (see Eq. (1)) are as follows:

$$\mathbf{B}(VII) = \begin{vmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}, \quad \mathbf{B}(VIII) = \begin{vmatrix} 0 & 0 & 0 \\ 1 & 0 & 1 \\ 0 & 0 & 0 \end{vmatrix} \quad (16)$$

and contain two unit elements in accordance with two C–C bonds present in both isomers (Numberings of $2p_z$ AOs are shown in Fig. 2).

Application of Eq. (4), in turn, yields

$$\mathbf{S}(VII) = -\mathbf{Q}(VII) = \mathbf{S}(VIII) = -\mathbf{Q}(VIII) = \frac{\gamma}{2} \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix},$$

$$\mathbf{R}(VII) = \frac{\gamma}{2} \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix},$$

$$\mathbf{R}(VIII) = \frac{\gamma}{2} \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{vmatrix}. \quad (17)$$

It is seen that the isomers VII and VIII are characterized by uniform blocks \mathbf{S} and \mathbf{Q} . Meanwhile, (sub)matrices $\mathbf{R}(VII)$ and $\mathbf{R}(VIII)$ differ one from another in signs of some off-diagonal elements. Because of the simple proportionality between matrices \mathbf{R} and $\mathbf{G}_{(1)}$ seen from Eq. (6), the same distinction refers also to the principal matrices $\mathbf{G}_{(1)}(VII)$ and $\mathbf{G}_{(1)}(VIII)$ [the latter evidently are particular cases of $\mathbf{G}_{(1)}(I)$ and $\mathbf{G}_{(1)}(II)$ of Eq. (11)]. Similarly, off-diagonal elements of opposite signs arise in the matrix products $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(VII)$ and $\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(VIII)$, viz.

$$\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(VII) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{vmatrix},$$

$$\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+(VIII) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{vmatrix}. \quad (18)$$

By contrast, the overall extent of dissimilarity of

matrices $\mathbf{G}_{(2)}(VII)$ and $\mathbf{G}_{(2)}(VIII)$ is much higher. Indeed, from Eqs. (6) and (17) we obtain

$$\mathbf{G}_{(2)}(VII) = \frac{\gamma^2}{8} \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{vmatrix}, \quad \mathbf{G}_{(2)}(VIII) = 0. \quad (19)$$

Thus, the distinction now consists in the non-zero and zero values, respectively, of elements $G_{(2)13}$ and $G_{(2)31}$, referring to BOs of the terminal bonds $C_1 = C_4$ and $C_3 = C_6$. To account for this important peculiarity, let us recall that matrix products \mathbf{SR} and $-\mathbf{RQ}$ ($=\mathbf{RS}$) of Eq. (6) are correspondingly responsible for mediating increments of BBOs and of ABOs to particular elements of the matrix $\mathbf{G}_{(2)}$ [see also Eq. (10) along with the discussion nearby and note that the product $-\mathbf{RQ}$ coincides with \mathbf{RS} due to the first relation of Eq. (4)]. For the isomers concerned, these products are as follows

$$\mathbf{SR}(VII) = \frac{\gamma^2}{16} \begin{vmatrix} -1 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{vmatrix}, \quad \mathbf{RS}(VII) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & -1 \end{vmatrix},$$

$$\mathbf{SR}(VIII) = \frac{\gamma^2}{16} \begin{vmatrix} -1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & -1 \end{vmatrix}, \quad \mathbf{RS}(VIII) = \frac{\gamma^2}{16} \begin{vmatrix} 1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & 1 \end{vmatrix}. \quad (20)$$

It is seen that contributions of products \mathbf{SR} and \mathbf{RS} to decisive elements $G_{(2)13}$ and $G_{(2)31}$ are of the same and of opposite signs for isomers VII and VIII, respectively. Hence, the mediating effects BOs $\varphi_{(+2)}$ and $\varphi_{(-2)}$ of the central bond $C_2 = C_5$ to the above-mentioned elements are added together (cancel out one another) for the linear (branched) hexatriene and this fact causes the distinction between matrices $\mathbf{G}_{(2)}(VII)$ and $\mathbf{G}_{(2)}(VIII)$ shown in Eq. (19). The same state of things evidently refers also to individual triplets of linear and cross-conjugated C=C bonds in extended polyenes.

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