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The matching of structural elements in reactions for evaluating stabilization energies for benzene and monosilabenzene

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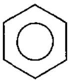
Using the 6-31G* basis set the stabilization energy for monosilabenzene has been calculated as ΔE_T for the homodesmotic reactions in which (i) ethylene is the other reactant with *trans* 1,3-butadiene and *trans* 2-sila-1,3-butadiene as the products, and (ii) *trans* 1,3-butadiene is the other reactant with *trans* 1,3,5-hexatriene and trans 3-sila-1,3,5-hexatriene as the products. The values are 17.2 and 17.6 kcal mol^{-1} respectively, compared to 24.8 and 23.5 kcal mol^{-1} respectively for the corresponding reactions of benzene. The difference is ΔE_T for the interchange of =SiH— and =CH— groups between the aromatic and aliphatic structural environments, and is thus more informative than the quotient. The extent of the matching of structural elements in these reactions, and in the benzene reactions using longer chain polyenes, is assessed in terms of the structural environment about each heavy atom in its entirety - namely the nearest neighbor atoms (NN), the next nearest neighbor atoms (NNN), and the more distant atoms (NNNN and NNNNN). Matching by number alone is designated "isoplesiotic", and if by both number and kind, "homoplesiotic".

Key words: Benzene - Monosilabenzene - Stabilization energy - Isoplesiotic - Homoplesiotic

1. Introduction

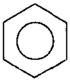
The methodology currently in use to assess the matching of structural elements in reactant and product molecules in organic reactions - especially those set up to evaluate stabilization energies for aromatic molecules - is based on comparisons of chemical bonding. In "isodesmic" bond separation reactions [1] there is minimal matching according to the number of formal single, double and triple bonds in the reactants and products. In "homodesmotic" reactions, which are a subclass of isodesmic reactions, there is further matching according to the number and type of carbon-carbon bonds (and carbon-heteratom bonds if present) and also to the number of hydrogen atoms bonded to each type of carbon atom C4, C3 and C2 (and each type of heteroatom if present) [2-7].

Extraneous energy contributions arising from the mismatch of structural elements can, for example, lead to widely differing values for the stabilization energy of benzene. Calculated as ΔH^0 from ΔH_f^0 data at 298 K [8], the isodesmic bond separation reaction



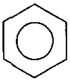
$$+ 6CH_4 \rightarrow 3H_3C{-}CH_3 + 3H_2C{=}CH_2 \qquad (1)$$

gives 64.2 ± 1.2 kcal mol^{-1}, compared to 21.6 ± 0.9 kcal mol^{-1} for the homodesmotic reaction [9]



$$+ 3H_2C{=}CH_2 \rightarrow 3\ \textit{trans}\ H_2C{=}CH{-}CH{=}CH_2 \qquad (2)$$

Many other homodesmotic reactions utilizing larger polyenes can be used for this purpose [10]. Those which involve in addition the matching of adjacent chemical bonds, e.g.

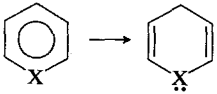
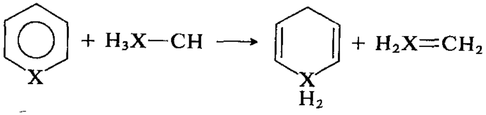
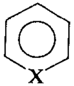
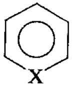
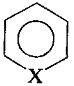


$$+ 3\text{-}\textit{trans}\text{-}H_2C{=}CH{-}CH{=}CH_2 \rightarrow 3\ \text{all-}\textit{trans}\text{-}H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2 \qquad (3)$$

have been termed "hyperhomodesmotic" [11], and are in turn a subclass of homodesmotic reactions. Another example of homodesmotic reactions that differ in the extent to which adjacent bonds are matched is provided by those which utilize either isobutene or 3-methylene-1,4-pentadiene to provide the quaternary carbon in the evaluation of stabilization energies for polycyclic benzenoid hydrocarbons [3].

Reactions analogous to (2) and (3) have been employed in the case of hexasilabenzene [12], but none of the reactions that have been used to compare the stabilization energies of monosilabenzene and benzene are homodesmotic, see Table 1a–c.

Table 1. Stabilization energies for benzene and monosilabenzene calculated as ΔE_T for various types of reaction

	Reaction	Reaction type	Basis set	Stabilization energy (kcal mol^{-1})
a.		anisodesmic [5]	STO-3G 3-21G*[a]	X=Si, 9.6 [13]: X=C 96.6 [14, 15] X=Si 18.0 [13]
b.	 $+ H_3X{-}CH \longrightarrow$ $+ H_2X{=}CH_2$	isodesmic [1]	STO-3G	X=Si, 22 [14]: X=C 32 [14]
c.	 $+5CH_4+XH_4 \rightarrow$ $2H_3C{-}CH_3+H_3X{-}CH_3+2H_2C{=}CH_2+H_2X{=}CH_2$	isodesmic bond separation [1]	STO-2G STO-3G 3-21G	X=Si, 61 [16]: X=C, 73 [16] X=Si, 60 [17]: X=C, 70 [17] X=Si, 47 [16]: X=C, 59 [16]
d.	 $+3H_2C{=}CH_2 \rightarrow$ 2 *trans*-$H_2C{=}CH{-}CH{=}CH_2$ + *trans*-$H_2C{=}XH{-}CH{=}CH_2$	homodesmotic [2, 3]	STO-3G 6-31G* (5D)	X=Si, 29.5[b]: X=C, 32.7 [15, 18, 19] S=Si, 17.2[b]: X=C, 24.8 [20, 21]
e.	 +3 *trans* $H_2C{=}CH{-}CH{=}CH_2 \rightarrow$ 2 *all trans*-$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$ + *all trans* $H_2C{=}CH{-}XH{=}CH{-}CH{=}CH_2$	hyperhomodesmotic [11]	6-31G* (5D)	X=Si, 17.6[b]: X=C, 23.5 [20, 21]

[a] 3-21G basis set augmented by a set of *d*-functions on the silicon (see [13] for details)

[b] This paper

Calculations have therefore been carried out on 2-sila-1,3-butadiene, 3-sila-1,3,5-hexatriene and monosilabenzene to evaluate ΔE_T for the monosilabenzene reactions corresponding to (2) and (3), i.e.,

$$\begin{aligned}\text{monosilabenzene} + 3H_2C{=}CH_2 \rightarrow\ & H_2C{=}SiH{-}CH{=}CH_2\\ & +2H_2C{=}CH{-}CH{=}CH_2 \qquad (4)\end{aligned}$$

and

$$\begin{aligned}\text{monosilabenzene} + 3H_2C{=}CH{-}CH{=}CH_2 \rightarrow\ & H_2C{=}CH{-}SiH{=}CH{-}CH{=}CH_2\\ & +2H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2 \qquad (5)\end{aligned}$$

In addition to the STO-3G basis set the 6-31G*(5*D*) basis set has also been employed so that comparison can be made with the most extended basis set data currently available for the benzene reactions [20, 21].

As an alternative to the characterization of reactions as anisodesmic, isodesmic, homodesmotic, etc., a different methodology has been worked out which is particularly suitable for reactions in which some of the molecules contain more than one kind of heavy atom, e.g., acyl derivatives, and for reactions involving the longer polyenes [22]. The matching of structural elements is assessed in terms of the structural environment about each heavy atom in its entirety, namely the nearest neighbor atoms and then the next nearest neighbor atoms and so on, and leads to reactions being designated as "isoplesiotic" and in some cases "homoplesiotic" at each structural level, depending on whether the matching is by number alone or by both number and kind. In the discussion this alternative methodology is employed,
(i) to show how the presence of the heteroatom in the monosilabenzene reactions affects the extent of the matching in relation to that in the benzene reactions, and
(ii) to establish the nature of the matching that is possible in the limit as longer and longer polyenes are used in the benzene reactions.

2. Computational details

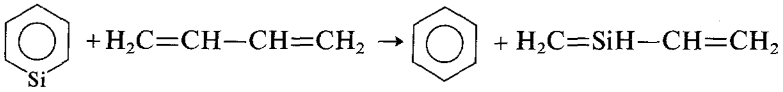
The calculations were carried out on a VAX 11/780 computer using the GAUSSIAN 82 program [23] and the STO-3G [24, 25] and 6-31G*(5D) [26, 27] basis sets with gradient optimization. In all cases the maximum forces on the distance and angle coordinates in the final optimization were less than 0.00045 hartree bohr^{-1} and 0.00045 hartree radian^{-1}.

For monosilabenzene it was assumed that the ring atoms and the H-atoms lie in the same plane, in accord with the finding of Schlegel et al. [14], otherwise full geometry optimization was employed for this molecule, for 2-sila-1,3-butadiene [28], and for 3-sila-1,3,5-hexatriene [29].

3. Results

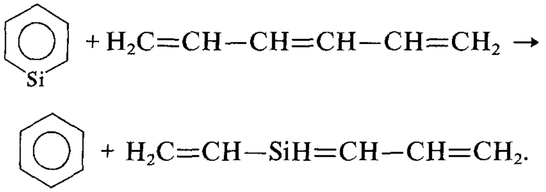
The calculated E_T values are as follows: STO-3G basis set, *trans* 2-sila-1,3-butadiene −401.17735 a.u.: 6-31G*(5D) basis set, *trans* 2-sila-1,3-butadiene −405.92623 a.u., *all trans* 3-sila-1,3,5-hexatriene −482.81181 a.u., and monosilabenzene −481.69757 a.u. The remaining E_T values needed to calculate the stabilization energies for reactions d and e in Table 1 were taken from the literature [14, 15, 18–21].

These values further support the conclusion that there is very considerable aromatic stabilization in monosilabenzene, viz 69% of the benzene value for reaction d and 75% for reaction e, compared to 69% and 80–84% for reactions b and c [14, 16]. However, in view of the composite nature of each individual ΔE_T (or ΔH^0) value, quotients such as these lack any direct correlation with structural properties of the aromatic molecule per se. In their place it is more instructive to consider the *difference* between the values. Whilst in the case of reactions a, b, and c these differences still reflect an intricate interplay between disparate structural elements besides the influence of aromatic stabilization, the difference in the case of reactions d and e amounts simply to ΔE_T for the interchange of the key structural elements —SiH= and —CH= between the aromatic and aliphatic (diene or polyene) structural environments, i.e.



(6)

and



(7)

The difference, −7.6 and −5.9 kcal mol^{-1} respectively, shows the interchange to be quite a favored process, in contrast to the corresponding diene reaction for pyridine for which ΔE_T is very small, less than 1 kcal mol^{-1} [6].

As the formal —CH= group in the aromatic structure is matched with —CH= groups in progressively longer polyenes, one would expect the stabilization energy to reach a constant value asymptotically. This is borne out for benzene by the ΔE_T values for the series of reactions with ethylene and butadiene (reaction 2), butadiene and hexatriene (reaction 3), hexatriene and octatetraene, and octatetraene and decapentaene. Calculations using 3-21G basis set data [11] give 27.6, 26.0, 25.5 and 25.4 kcal mol^{-1} respectively, and 6-31G basis set data [20, 21] 27.7, 26.2, 25.7 and 25.5 kcal mol^{-1} respectively. The values for reactions (2) and (3) at the 6-31G*(5D) level, see reactions d and e in Table 1, follow the same trend. But whereas this trend is towards a slightly lower value, that for monosilabenzene, insofar as the values for the reactions at the 6-31G*(5D) level

Table 2. Classification of reactions according to the isoplesiotic and homoplesiotic criteria

	NN		NNN	
Class	isoplesiotic	homoplesiotic	isoplesiotic	homoplesiotic
i	no	no	no	no
ii	yes	no	no	no
iii	yes	no	yes	no
iv	yes	yes	yes	no
v	yes	yes	yes	yes

can be taken as a guide, is towards a slightly higher value. In the limit, rough extrapolations give 22.6 and 17.9 kcal mol^{-1} for benzene and monosilabenzene respectively.

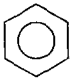
4. Discussion

The procedure [22] for assessing the matching of structural elements according to the nearest neighbor (NN) and next nearest neighbor atoms (NNN) about the heavy atoms is as follows. If there is the same number of each kind of heavy atom with the same number of NN atoms in the products as in the reactants, the reaction is designated "isoplesiotic", while if there is the same number of each kind of heavy atom with both the same number and the same kind of NN atoms in the product as in the reactants, the reaction is designated "homoplesiotic"* at this level, likewise at the NNN level, and more distant levels as needed [30]. Homoplesiotic reactions are thus a subclass of isoplesiotic reactions, just as homodesmotic reactions are a subclass of isodesmic reactions.

Taking the NN and NNN levels together, five classes of reaction can be distinguished according to the extent of the matching, see Table 2; and, even though a particular reaction may not meet the isoplesiotic (or homoplesiotic) criterion in full, a greater fraction of the heavy atoms may be matched than in another closely related reaction.

The NN and NNN atoms around each heavy atom in acetylene and in the molecules involved in reactions c, d and e in Table 1 are listed in Table 3. The specification of NNN atoms (and later the NNNN and NNNNN atoms) is made on the basis of the "through-bond" framework, and not on the actual distances, "through-space", between the reference atom and the other atoms in its vicinity [34].

The characteristic feature of anisodesmic hydrocarbon reactions is a mismatch in the connectivity of the carbon, as exemplified by the fission of benzene,



$$\rightarrow 3HC{\equiv}CH \qquad (8)$$

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[1] Derived from the Greek adjective "plesios" meaning near, close, neighboring. Isoplesiotic thus suggests equality among neighbors, i.e. in magnitude, hence by number alone: whereas homoplesiotic suggests sameness among neighbors, i.e., by both number and kind

in which C3 carbons become C2 carbons in the product. Reference to the NN and NNN assignments in the table shows this to be a class (i) reaction. Reaction a in Table 1, which is also anisodesmic, is likewise a class (i) reaction. In reaction b the connectivity is now matched with C4 (or Si4), 6C3 and C2 (or Si2) in both products and reactants, and as a consequence the reaction is isodesmic. The NN and NNN assignments show it to come into class (ii). This is also the case for reaction c, which is isodesmic both with $X=C$ and $X=Si$. Reaction d, on the other hand, is homodesmotic, and the assignments show it to be isoplesiotic at both the NN and NNN levels with $X=C$ and $X=Si$. With $X=C$ it is homoplesiotic at the NN level, but there is no homoplesiotic matching at the NNN level and the reaction thus comes into class (iv). However with $X=Si$ the presence of the heteroatom reduces the matching significantly. Only 10/12 of the heavy atoms at the NN level are matched according to the homoplesiotic criterion, and the reaction reverts to class (iii). A similar feature is found in reaction e. The more extensive matching resulting from the utilization of the diene and triene leads to the reaction with $X=C$ meeting the homoplesiotic criterion at both the NN and NNN levels, and it is thus a class (v) reaction: whereas with $X=Si$ only 14/18 of the heavy atoms are matched according to the homoplesiotic criteria, and the reaction reverts to class (iv). For easy comparison these findings are brought together in Table 4.

With regard to the benzene reactions in which the longer chain polyenes are employed, it has been shown [22] that just as the reaction with butadiene and hexatriene is homoplesiotic at both NN and NNN levels so are the reactions with hexatriene and octatetraene, and with octatetraene and decapentaene, as might be expected. Hence, although the ΔE_T values still show a small but perceptible decrease, this is not reflected in the matching thus far. In going to the next (NNNN) level, however, a drastic reduction in the matching occurs. None of the reactions are even isoplesiotic. This comes about because there is an irreducible mismatch between the carbon atoms of benzene, for which the NNNN atoms are [C3, 2H], and the carbon atoms of the polyenes, for which the NNNN atoms are [C3, H] for C_1 and C_2, [C3, 3H] for C_3, and [2C3, 2H] for C_4, C_5 etc. irrespective of chainlength.[2] Thus the best matching that can be achieved still leaves 6C3[C3, 2H] on the reactant side and 6C3 [2C3, 2H] on the product side. The same is true for reactions in which the CH groups from the benzene are restructured as the chain CH groups in a single long chain polyene [10, 22] e.g.,

$$\text{benzene} + \text{hexatriene} \rightarrow \text{dodecahexaene}$$

(see note 35).

At the NNNNN level an irreducible mismatch in the benzene reactions is yet more obvious. For benzene there is only one NNNN atom, i.e., [H], while for the long chain polyenes the NNNNN atoms for C_5, C_6, etc., are the same as the NNNN atoms atoms for C_4, C_5, etc., i.e., [2C3, 2H].

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[2] Using the numbering system [20], $C_1{=}C_2{-}C_3{=}C_4{-}C_5{=}C_6{\cdots}C_{6'}{=}C_{5'}{-}C_{4'}{=}C_{3'}{-}C_{2'}{=}C_{1'}$

Table 3. Checklist of nearest neighbor (NN) and next nearest neighbor atoms (NNN)[a]

Molecule	Reference atom[b]	NN	NNN
Methane (Silane)	C (Si)	4H	none
Acetylene	C	C2, H	H
Ethylene	C	C3, 2H	2H
Ethane	C	C4, 3H	3H
1,3-Butadiene	C_1	C3, 2H	C3, H
	C_2	2C3, H	C3, 3H
1,3,5-Hexatriene	C_1	C3, 2H	C3, H
	C_2	2C3, H	C3, 3H
	C_3	2C3, H	2C3, 2H
Benzene	C	2C3, H	2C3, 2H
Silaethylene	C	Si3, 2H	2H
	Si	C3, 2H	2H
Silaethane	C	Si4, 3H	3H
	Si	C4, 3H	3H
2-Sila-1,3-butadiene	C_1	Si3, 2H	C3, H
	Si_2	2C3, H	C3, 3H
	C_3	C3, Si3, H	C3, 3H
	C_4	C3, 2H	Si3, H
3-Sila-1,3,5-hexatriene	C_1	C3, 2H	Si3, H
	C_2	C3, Si3, H	C3, 3H
	Si_3	2C3, H	2C3, 2H
	C_4	C_3, Si3, H	2C3, 2H
	C_5	2C3, H	Si3, 3H
	C_6	C3, 2H	C3, H
Monosilabenzene	Si_1	2C3, H	2C3, 2H
	C_2	C3, Si3, H	2C3, 2H
	C_3	2C3, H	C3, Si3, 2H
	C_4	2C3, H	2C3, 2H

[a] The connectivity of the C- and Si-atoms is denoted by the number after the symbol

[b] The subscripts indicate the position of the atom in the chain or ring

Table 4. Classification of reactions a - e in Table 1

		NN		NNN		
Reaction	X	isoplesiotic	homoplesiotic	isoplestiotic	homoplesiotic	Classification
a	C	no	no	no	no	i
	Si	no	no	no	no	i
b	C	yes	no	no	no	ii
	Si	yes	no	no	no	ii
c	C	yes	no	no	no	ii
	Si	yes	no	no	no	ii
d	C	yes	yes	yes	no	iv
	Si	yes	no (10/12)[a]	yes	no	iii
e	C	yes	yes	yes	yes	v
	Si	yes	yes	yes	no (14/18)[a]	iv

[a] The fractions in parentheses give the extent to which the heavy atoms are matched even though the homoplesiotic criterion is not met in full

Thus, even in the limit, some small energy contribution from this distant mismatch of structural elements is unavoidable. However, the very small increment in ΔE_T noted above as one goes up the series beyond the butadiene and hexatriene reaction show it to be more of theoretical significance than practical importance, or to generalize, this alternative methodology provides a very convenient way to make a precise correlation between the mismatch of structural elements and their influence on reaction energies.

References

1. Hehre WJ, Ditchfield R, Radom L, Pople JA (1970) J Am Chem Soc 92:4796
2. George P, Trachtman M, Bock CW, Brett AM (1975) Theor Chim Acta 38:121
3. George P, Trachtman M, Bock CW, Brett AM (1976) J Chem Soc Perkin Trans 2:1222
4. George P, Trachtman M, Bock CW, Brett AM (1976) Tetrahedron 32:1357
5. George P, Trachtman M, Brett AM, Bock CW (1977) J Chem Soc Perkin Trans 2:1036
6. George P, Bock CW, Trachtman M (1985) Tetrahedron Lett 26:5667
7. George P, Bock CW, Trachtman M (1982) The evaluation of stabilization energies (Empirical Resonance Energies) for benzene, porphine and [18] annulene from Thermochemical Data and Ab Initio Calculations. In: Dunford B, Dolphin D, Raymond K, Sieker L (eds) The biological chemistry of iron. Reidel, Boston, p 276
8. Pedley JB, Rylance J (1977) Sussex-NPL Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex
9. It should perhaps be emphasized that what is at issue is not the shift of a baseline from which the stabilization energy of benzene and other molecules is measured, but that the choice of reaction affects the relative magnitudes selectively. For example, the value for [18] annulene according to the reaction analogous to (1) is $+127.9 \pm 8.7$ kcal mol^{-1}, i.e., twice that for benzene, whereas the value according to the reaction analogous to (2) is -1.1 ± 7.8 kcal mol^{-1}, suggesting there is very little if any stabilization [7]
10. See [4], footnote g Table 1
11. Hess BA, Schaad LJ (1983) J Am Chem Soc 105:7500
12. Nagase S, Kudo J, Aoki M (1985) J Chem Soc Chem Commun 1121

13. Chandrasekhar J, Von Rague Schleyer P, Baumgartner ROW, Reetz MT (1983) J Org Chem 48:3453
14. Schlegel HB, Coleman B, Jones M Jr (1978) J Am Chem Soc 100:6499
15. Von Nagy-Felsobuki E, Topsom RD, Pollack S, Taft RW (1982) Theochem 88:255
16. Gordon MS, Boudjouk P, Anwari F (1983) J Am Chem Soc 105:4972
17. Hehre WJ, Radom L, Von R Schleyer P, Pople JA (1986) *Ab initio* molecular orbital theory. Wiley Interscience, New York, Table 7.16, p 375
18. Latham WA, Hehre WJ, Pople JA (1971) J Am Chem Soc 93:808
19. Hehre WJ, Pople JA (1975) J Am Chem Soc 97:6941
20. Bock CW, George P, Trachtman M (1984) Theochem 109:1
21. Bock CW, George P, Trachtman (1984) J Phys Chem 88:1467
22. George P, Bock CW, Trachtman M: Empirical resonance energies of acyl and carbonyl derivatives. In: Greenberg A, Liebman JF, (eds) Molecular structures and energetics, vol 4, chap 5. Verlag Chemie International, Deerfield Beach, Florida (in press)
23. Binkley JS, Frisch M, DeFrees DJ, Raghavachari K, Whiteside RA, Schlegel HB, Fluder EM, Pople JA (1982) Carnegie-Mellon University, Pittsburgh 15213
24. Hehre WJ, Ditchfield R, Pople JA (1970) J Chem Phys 52:2769
25. Gordon MS, Bjorke MD, Marsh FJ, Korth NS (1978) J Am Chem Soc 100:2670
26. Hariharan PC, Pople JA (1973) Theor Chim Acta 28:213
27. Francl MM, Pietro WJ, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, Pople JA (1982) J Chem Phys 77:3654
28. Trinquier G, Malrieu J-P (1981) J Am Chem Soc 103:6313
29. The geometry, charge distribution and overlap populations will be reported elsewhere, and comparisons made with data for the nitrogen analogs and parent hydrocarbons at the 6-31G*(5D) level
30. This formalism differs from that employed in "bond energy analysis" in which E_T is decomposed into one-, two-, three- and four-center energies [31-33]
31. Clementi E (1967) J Chem Phys 46:3842
32. Clementi E (1969) Int J Quantum Chem III s:179
33. Clementi E, Von Niessen W (1971) J Chem Phys 54:521
34. For benzene, ethylene and the all trans polyenes the distance matrices obtained using the 6-31G basis set give the same assignments. There is a clear-cut separation between the NN, NNN, NNNN and NNNNN levels. For benzene the distances are 1.0733 – 1.3883 Å, 2.1376 – 2.4045 Å, 2.7765 – 3.3770 Å and 3.8498 Å respectively, and for all trans hexatriene (which is typical of the longer all trans polyenes) 1.0724 – 1.4598 Å, 2.0807 – 2.4700 Å, 2.6900 – 3.8320 Å and 4.0211 – 4.9372 Å respectively. For some polyenes in which there are *cis* structural elements this would no longer be the case.
35. The severity of the constraint imposed by the homoplesiotic criterion at the various levels is evident from the shortest chain polyenes needed to meet the criterion in the disproportionation reaction, i.e.,

    NN level

    butadiene + octatetraene → 2 hexatriene

    NNN level

    hexatriene + decapentaene → 2 octatetraene

    NNNN level

    octatetraene + dodecahkexaene → 2 decapantaene