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Anticipating Semiempirical π -bond Dispositions in Cyclic, Even, Classical Hydrocarbons

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 π -bond placement coefficients.

Abstract

A new technique, which employs π -bond placement coefficients, is presented. That technique, in conjunction with a few parameters which are readily available from traditional Hückel theory, permits one to systematically anticipate PM3 calculated π -bond placements for optimized lowest-lying singlet states. One may then foresee the relative magnitudes of PM3 calculated ΔH_f values for selected sets of structural isomers.

Introduction

Traditional (i.e. Zeroth Order) Hückel calculations produce descriptions for classical, even hydrocarbons by optimizing π -electron energies exclusively. In contrast, realistic descriptions must allow for structural effects owing to other factors e.g. Coulombics, ring strain and steric crowding. Useful comparisons of structural descriptions at the Hückel and PM3 semiempirical levels of theory may employ π -bond orders (p_{ij}) and π -system derived partial positive charges (Σ_{q+}).^[1,2] Whenever a traditional Hückel description fails to provide reasonable agreement with the corresponding semiempirical description, there can be no rational basis for an expectation that key frontier orbital energies will correlate. Figure 1 provides one of many examples of significant divergence (both p_{ij} and Σ_{q+}) between traditional Hückel and semiempirical descriptions for a simple classical hydrocarbon.

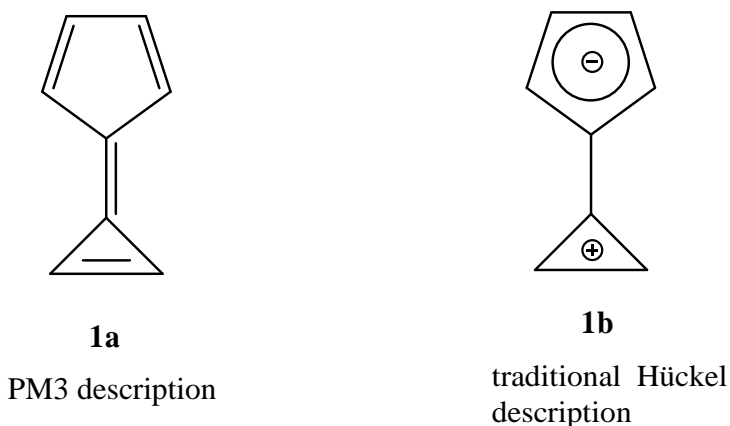


Fig. 1. Conflicting descriptions for cyclopropyl cyclopentadiene. The Σ_{q+} values for the π -system are 0.2413 (PM3) and 0.8240 (Hückel). The π -bond orders for the bond connecting the two rings are 0.8321 (PM3) and 0.4436 (Hückel).

Figure 2 presents a set of common, classical hydrocarbons **2** → **7**. Figure 3 provides a plot of traditional Hückel Highest Occupied Molecular Orbital (HOMO) eigenvalues against the corresponding PM3 values for those classical hydrocarbons.

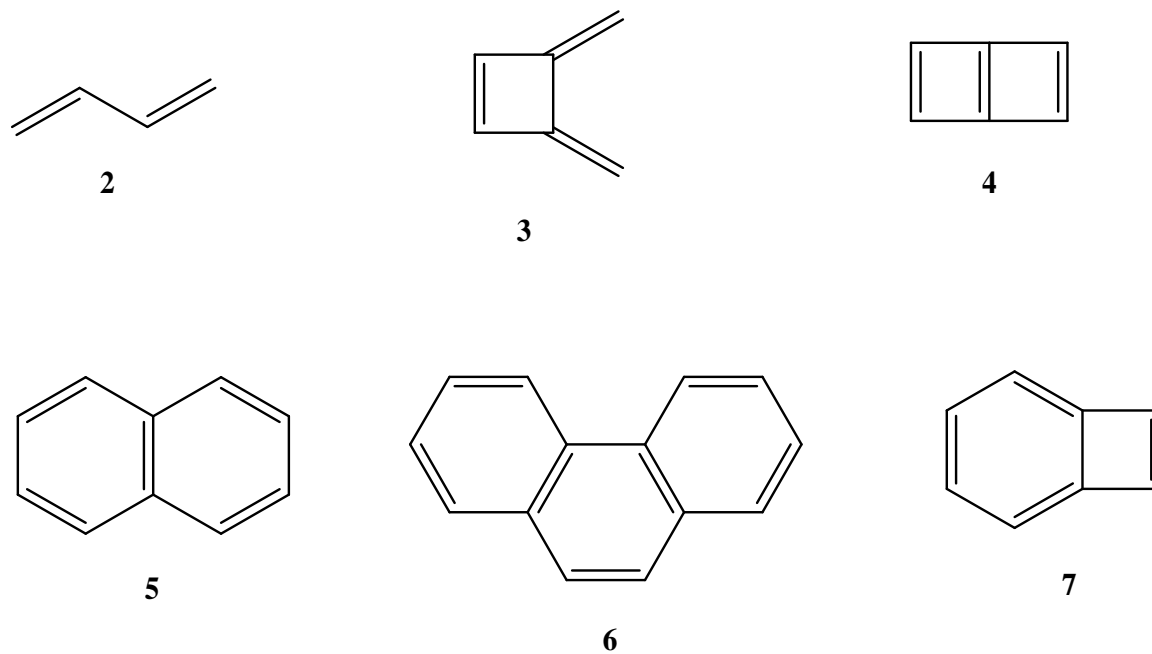


Fig. 2. Classical hydrocarbon structures for Fig. 3.

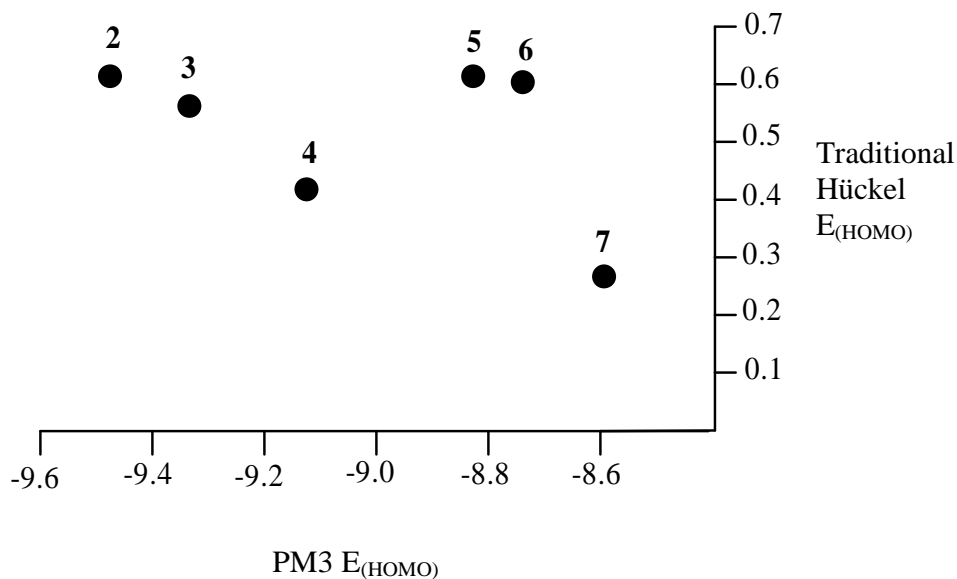


Fig. 3. A plot of PM3 HOMO eigenvalues (eV) against traditional Hückel HOMO eigenvalues (β units). The plot has an R^2 value of 0.19 which indicates little correlation between the two sets of numbers. The structures **2** \rightarrow **7** are given in Fig. 2.

Given the results in Figures 1 and 3 along with the assumption that, for interesting pairs of classical hydrocarbons, it is the relative values of PM3 eigenvalues that is the more realistic, it is clear that more realistic Hückel structural descriptions are a prerequisite for more realistic Hückel energies.

Recently, we have developed a Chemical Graph Theoretical approach that permits one to anticipate relative HOMO energies (E_H , traditional Hückel level) for even, alternant, classical hydrocarbons.^[3] Without a substantial improvement in Hückel level descriptions, our simple Chemical Graph Theoretical approach to anticipating relative reactivities for even, alternant hydrocarbons will only provide unrealistic relative E_H estimates.

For these reasons, we have undertaken work intended to develop a simple technique that would permit one to anticipate semiempirical π -bond placements on even, classical hydrocarbon frameworks. Such information, should facilitate judicious selection of κ_{ij} values (Bond Integral

coefficients) which in turn could lead to more realistic Hückel structures. Graph Theoretical treatments, informed by more realistic Hückel descriptions, would be empowered in an unprecedented manner.

The current report develops simple guidelines that allow anticipation of PM3 calculated π -bond placements for both alternant and non-alternant even, classical hydrocarbons.

Methods

PM3 computations were carried out as described earlier.^[4] A brief comparison of PM3 calculated bond lengths and dipole moments with AM1 calculated and experimental results has been provided previously.^[5]

Recognizing Even, Alternant, Classical Hydrocarbons That May Have NBMOs

At the Hückel level, a structure for which $S_n \neq \emptyset$ can only have a non-bonding molecular orbital (NBMO) if it has two sets of s_n subgraphs which lead to $(a_n)_{\text{part}}$ values that are equal in magnitude but opposite in sign. For alternant hydrocarbons, both acyclic s_n subgraphs and those whose cyclic components are restricted to $4N+2$ circuits lead to increased $|a_n|$. Only s_n subgraphs that contain an odd number of $4N$ circuits lead to decreased $|a_n|$. Hence, any even, classical, alternant hydrocarbon structure ($S_n \neq \emptyset$) that is ascribed NBMOs by traditional Hückel calculations has s_n subgraph(s) which feature an odd number of $4N$ circuits. Those elementary $4N$ circuits may be associated with elementary rings or non-elementary rings (fused ring perimeters) e.g. the ApB circuit^[6] for benzocyclobutadiene **7**.

Consider fused bicyclic perimeters. When a $4N+2$ ring is fused to a $4N+2$ ring and the perimeter allows an ApB circuit, that perimeter must be a $4N+2$ elementary circuit. When a $4N+2$ ring is fused to a $4N$ ring and the perimeter allows an ApB circuit, that perimeter must be an elementary $4N$ circuit. When a $4N$ ring is fused to a $4N$ ring and the perimeter allows an ApB

circuit, that perimeter must be an elementary $4N+2$ circuit. From this point it is easy to see that no even, alternant, classical hydrocarbon can have a $4N$ fused polycyclic perimeter which serves as a valid circuit in an s_n subgraph unless that structure has an elementary $4N$ ring in its Lewis structure. Thus, any even, classical, alternant hydrocarbon must have at least one elementary $4N$ ring in its Lewis structure, if the traditional (Zeroth Order) Hückel description attributes NBMOs to it. Note that the converse is untrue. Only those classical, alternant hydrocarbons that feature one or more $4N$ rings merit further scrutiny to see whether they have NBMOs at the Hückel level.

Glossary

1. Σ_{q+} is obtained, from traditional Hückel calculations, by summing the partial positive charges derived from the π -system.
2. A classical Lewis structure is fully π -bonded i.e. it shows no dots.
3. The Bond Integral Coefficient (κ_{ij}). Molecular orbital computations employ Bond (or Resonance) Integrals^[7] which have the form given in eqn [1].

$$\int p_i H p_j dv \equiv H_{ij} \quad [1]$$

At the Hückel level, H_{ij} is defined as shown in eqn [2].

$$H_{ij} = \kappa_{ij}\beta \quad [2]$$

Traditional Hückel calculations, on hydrocarbons, set all κ_{ij} equal to one.

4. Traditional Hückel calculations construct and diagonalize a secular determinant for each hydrocarbon of interest. Chemical Graph Theory enumerates Sachs' subgraphs and then

employs the Sachs' formula for each subject hydrocarbon. Each approach produces a polynomial (see Eqn [3]).

$$a_0x^n + a_1x^{n-1} + \dots + a_{n-1}x + a_n = 0 \quad [3]$$

Traditional Hückel calculations produce the secular equation while Chemical Graph Theory produces the characteristic polynomial. Each polynomial leads to the Hückel level eigenfunctions and eigenvalues of interest. Given one polynomial, the other polynomial can be obtained by reversing the sign of each odd coefficient i.e. a_1, a_3, \dots ^[8]

5. A Sachs' subgraph is a construct elaborated on the molecular framework. Components may be circuits (elementary) or σ bonds. Components may not be incident (contiguous).^[6]

6. A dense Sachs' subgraph is a construct elaborated on the molecular framework. In general, components are odd or even alternant (or non-alternant) hydrocarbons. For alternant subject molecules, $|a_n|$ and $|a_{n-1}|$ values for each odd component are shown adjacent to that component in the dense Sachs' subgraph. Moreover, for alternant subject molecules, $|a_n|$ and $|a_{n-2}|$ values for each even component are shown adjacent to that component in the dense Sachs' subgraph.^[6]

7. An elementary circuit is unbridged i.e. each vertex in that circuit has exactly two closest neighbors that are also in that same circuit.^[9] An elementary ring is unbridged in the Lewis structure and is what is commonly meant when experimentalists use the word ring.

8. A non-alternant hydrocarbon for which $\Delta \neq 0$ has unequal numbers of bonding and antibonding orbitals at the Hückel level. Such structures are expected to be chemically unstable.

Results and Discussion

Pronounced π -Bond Localization in Classical Acyclic and Non-alternant π -Systems

The dominant imperative for anticipating relative PM3 calculated π -bond placements is the well-known Lewis octet rule. Hence, descriptors for neutral, classical hydrocarbons in which individual carbon atoms bear a charge, will not be further employed in the present discussion. Application of the Lewis octet rule leads to the conclusion that many even, classical hydrocarbons have a single pictorial representation which locates short (double) CC bonds and long (single) CC bonds unambiguously. Hexatriene **8** will serve as a simple example (see Fig. 4).

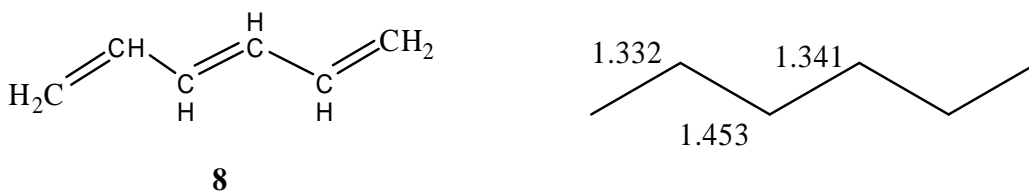


Fig. 4. A Lewis structure and PM3 calculated CC bond lengths (\AA) for the lowest-lying singlet state of hexatriene **8**.

At the Hückel level, the traditional description of hexatriene does not attribute NBMOs to the structure (alternant hydrocarbon that has no $4N$ rings in its Lewis structure, see Methods). Alternately, this conclusion may be reached by establishing that $|a_n| \neq 0$ (a_n is the tail coefficient in the secular equation). When $|a_n| \neq 0$ for an even, alternant, classical hydrocarbon, the PM3 calculated description of the Lewis structure will have the most symmetry permitted by the molecular topology. The foregoing generalization facilitates the effort to anticipate π -bond placements in the target molecules of current interest.

The best-known example of a structure that lacks the bond-length alternation featured in the Lewis structure of hexatriene **8** (Fig. 4) is benzene **9** (see Fig. 5).

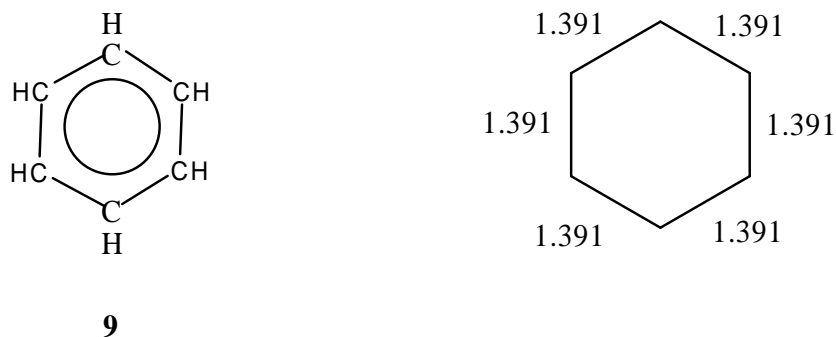


Fig. 5. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of benzene **9**.

Of course, the absence of CC bond-length alternation in benzene **9** can be anticipated by means of Kekulé contributors (see Fig. 6).

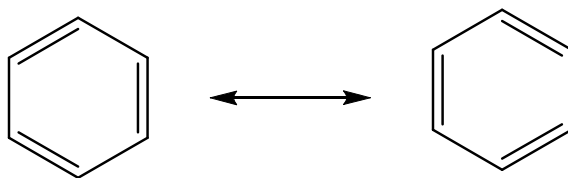


Fig. 6. Kekulé contributors for benzene **9**.

The presence of one or more rings in a hydrocarbon π -system does not always minimize π -bond localization. In some cases that can be deduced by application of the Lewis octet rule (see Fig. 7).

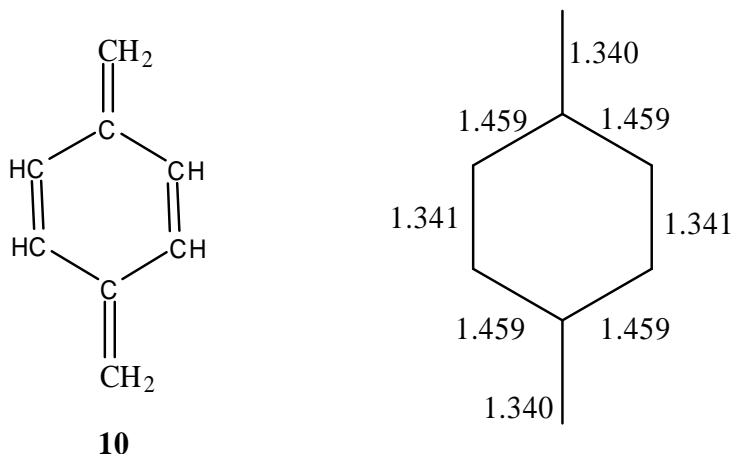


Fig. 7. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of *p*-quinodimethane **10**.

Now consider the simple even non-alternant hydrocarbon **11** (see Fig. 8).

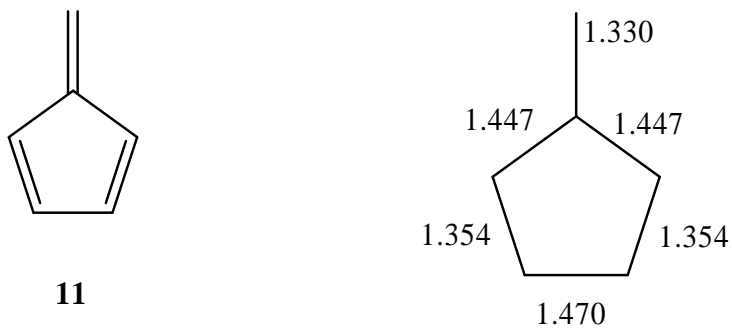


Fig. 8. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of methylene cyclopentadiene **11**.

For structure **11** (Fig. 8), as for structure **10** (Fig. 7), π -bond placements are obvious on the basis provided by the Lewis octet rule.

Although **11** has a unique representation, it is not unusual for non-alternant hydrocarbons to have Kekulé contributors available (see Fig. 9).

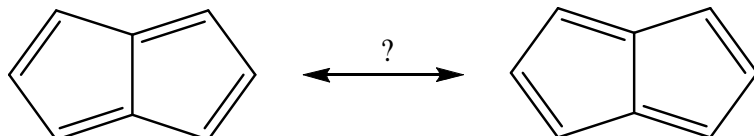


Fig. 9. Possible Kekulé contributors for pentalene **12**.

If the contributors for pentalene **12** (Fig. 9) are weighed equally (same procedure as employed for benzene's contributors [Fig. 6]), one would expect a long central bond and shorter peripheral bonds of similar lengths. PM3 calculated bond lengths militate against such a view (see Fig. 10).

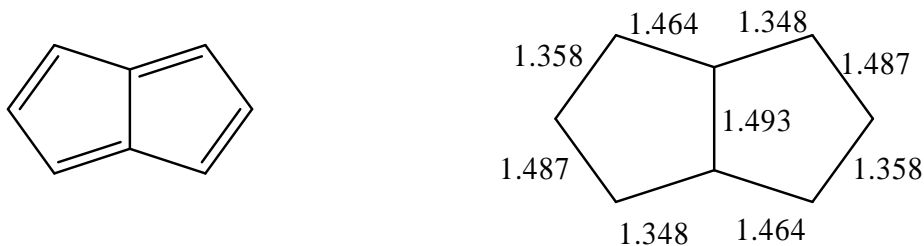


Fig. 10. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of pentalene **12**.

In sharp contrast to the expectation for **12** based on either the Kekulé contributors or traditional Hückel calculations which provide three bond lengths, the PM3 description provides five bond lengths. The pair of symmetry planes (perpendicular to the molecular plane) evident in the Hückel results for **12** are absent from the PM3 description shown in Fig. 10.

Generally, optimized PM3 descriptions for the lowest-lying singlet states of even, classical, non-alternant hydrocarbons exhibit pronounced π -bond localization. Commonly, Kekulé contributors for non-alternant hydrocarbons are misleading, if PM3 results are the standard, when they imply π -bond delocalization.

A single Lewis structure for pentalene **12** (see Fig. 10) gives the preferred view of **12**. Hence, routine structural considerations for non-alternant elementary rings should not rely on the use of Kekulé contributors.

π -Bond Delocalization: Selected Alternant and Non-alternant Polycycles

The best-known hydrocarbon structure that has π -bond delocalization is that of benzene **9** (see Figs. 5, 6). Benzene, with its perfect delocalization, is a unique monocycle. PM3 computational results also provide similar descriptions for structures having C_6 circuits of the ApB or ApBpC type.^[6]

Consider the even, alternant hydrocarbon bicyclo[2.2.0]hexatriene **4** which has the Kekulé contributors shown in Fig. 11.

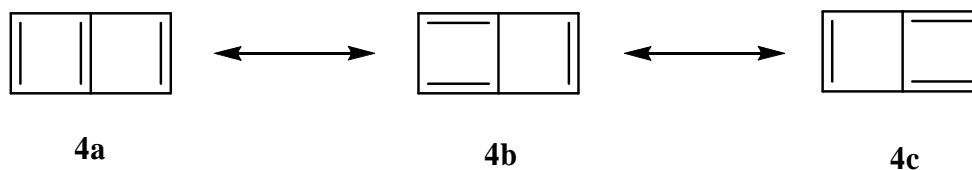


Fig. 11. Kekulé contributors for bicyclo[2.2.0]hexatriene **4**.

Note that PM3 calculations should and do provide **4** with the maximum symmetry allowed by its topology. As mentioned earlier, that result can be deduced by ascertaining that, at the Hückel level, the absolute value of the tail coefficient, $|a_n|$ (in either the secular equation or the characteristic polynomial), is not zero which can be done quickly by means of dense Sachs subgraphs.^[6]

Employing the Kekulé contributors for **4**, no matter what the non-zero ratios selected for **4a**, **4b** and **4c**, leads to the conclusion that the end bonds must be the shortest bonds in the structure. PM3 results (Fig. 12) are incompatible with that expectation.

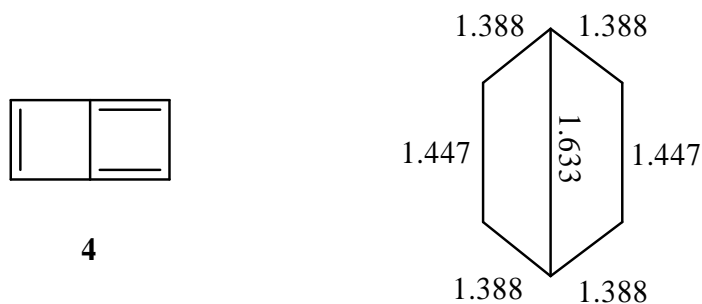


Fig. 12. A traditional Lewis structure and PM3 calculated CC bond lengths for the lowest-lying singlet state of bicyclo[2.2.0]hexatriene **4**.

Since no manipulation of the Kekulé contributors for **4** will lead to the PM3 description, some other approach is necessary. Assuming that the frontier orbitals will provide insight into preferred bond lengths *for small molecules*, we have constructed the partial correlation diagram shown in Fig. 13.

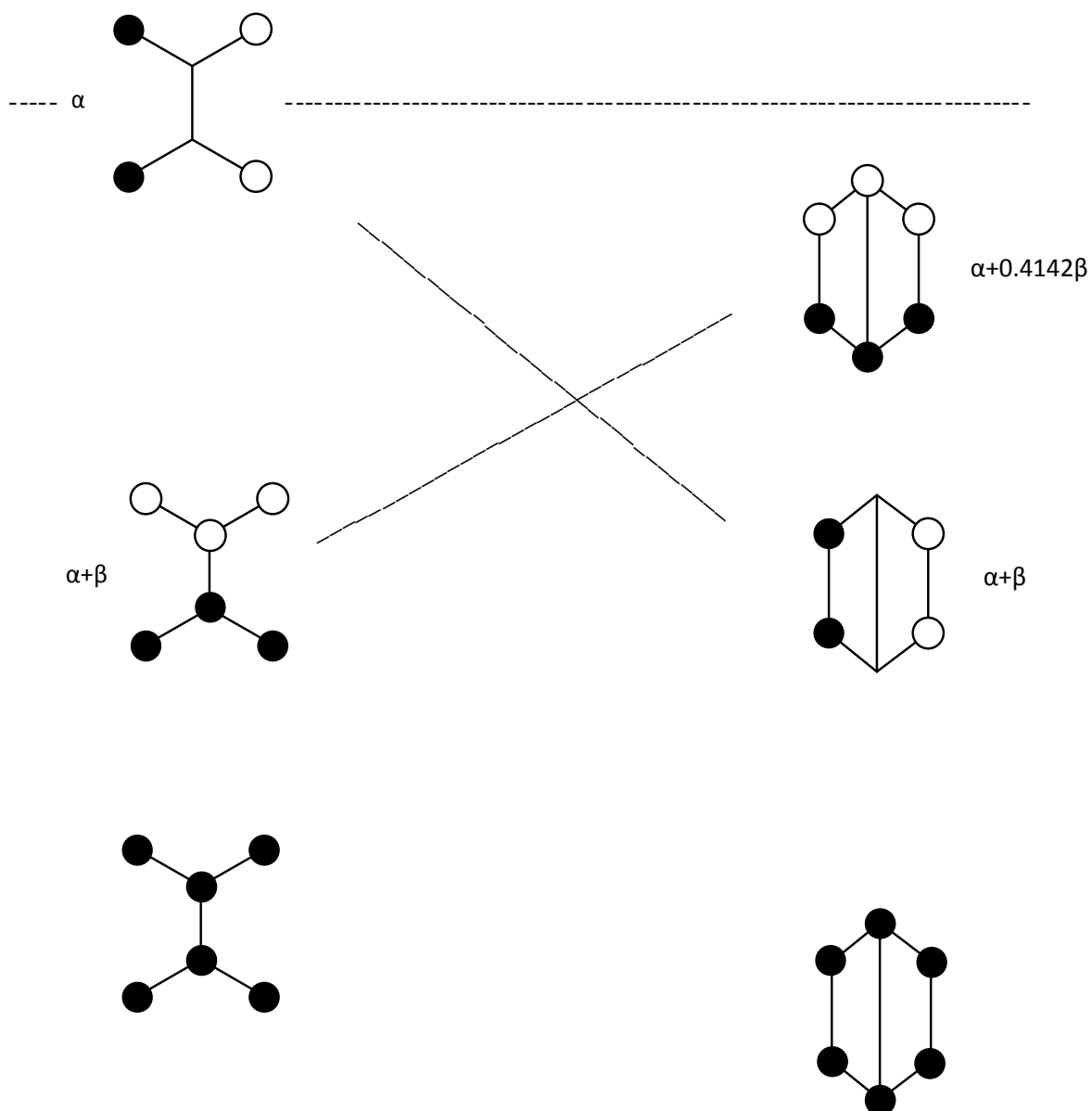
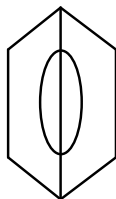


Fig. 13. A partial correlation diagram for the conversion of the tetramethylene ethane π -system into the bicyclo[2.2.0]hexatriene **4** π -system (relative magnitudes of non-zero coefficients not shown).

The nodal properties of the HOMO of **4**, given in the correlation diagram in Fig. 13, rationalize the bond length patterns in Fig. 12 smoothly. Furthermore, once one appreciates that Ψ_2 and Ψ_3

for tetramethylene ethane give rise to product orbitals with reversal of their relative energies, the bond length patterns in Fig. 12 can be directly anticipated from Ψ_2 of tetramethylene ethane.

The failure of the PM3 calculated peripheral bond lengths to alternate, as they are known to do in cyclobutadiene,^[10] may be taken as support for the need to deploy a different structural notation for bicyclo[2.2.0]hexatriene **4** (see Fig. 14).



4

Fig. 14. A proposed structural notation for bicyclo[2.2.0]hexatriene **4**.

PM3 calculations on bicyclo[3.1.0]hexatriene **13** and tricyclo[3.1.0.0^{2,4}]hexatriene **14** give particularly interesting results. Both molecules are non-alternant, suggesting peripheral bond-length alternation (like pentalene **12** [Fig. 10]). On the other hand, each has a C₆ perimeter [like benzene **9** (Fig. 5) and bicyclo[2.2.0]hexatriene **4** (Fig. 12)] suggesting greater π -bond delocalization and increased symmetry for **13** and **14**. PM3 results (see Fig. 15) allocate the higher symmetry structures to **13** and **14** and avoid the alternating bond lengths typical of most non-alternant hydrocarbon semiempirical descriptions.

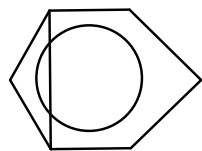
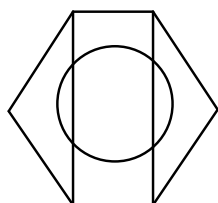
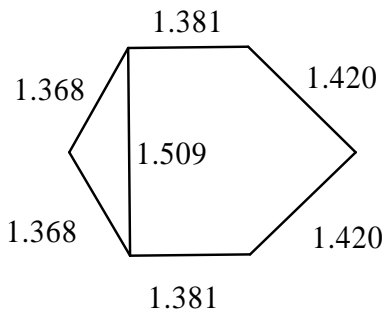
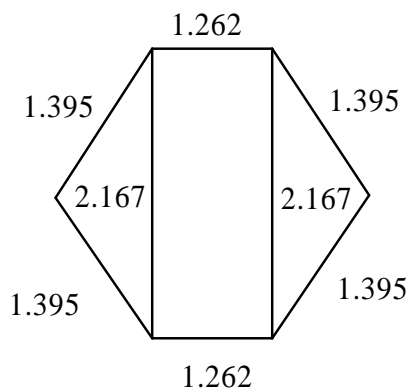
**13****14**

Fig. 15. Lewis structures for bicyclo[3.1.0]hexatriene **13** and tricyclo[3.1.0.0^{2,4}]hexatriene **14** and PM3 calculated bond lengths (in Angstroms) for their lowest-lying singlet states.

Like the results for **4** (Fig. 12), the polycycles **13** and **14** (Fig. 15) have long ring junctures and peripheral bond lengths that do not alternate, hence the same Lewis structure convention has been employed for all three structures.

Selected Hydrocarbons (C₄ Rings Exclusively): π -Bond Localization vs π -Bond Delocalization

In sharp contradistinction to benzene **9** (Fig. 5), the four-carbon annulene, cyclobutadiene **15**, is predicted to have a lowest-lying singlet state which features pronounced π -bond localization (see Fig. 16).

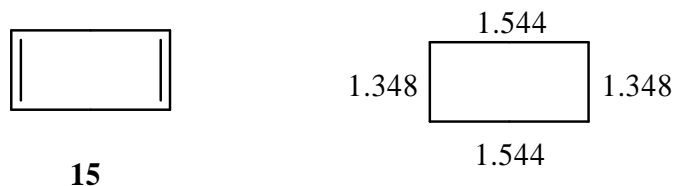


Fig. 16. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of cyclobutadiene **15**.

Although the distortion from a regular polygonal structure for **15** is widely attributed to Jahn-Teller distortion, Bally and Masamune have argued against that rationale.^[10]

One might now expect, like **15**, that classical alternant Lewis structures which feature one or more C₄ rings would consistently show bond-length alternation in optimized PM3 descriptions. While the bicyclohexatriene **4** does not, we have argued that it is a special case on account of its C₆ perimeter. An examination of the PM3 results for tricyclo[4.2.0.0^{2,5}]octatetraene **16** (see Fig. 17) offers nice support for that contention. Note that traditional Hückel results provide a non-zero value for the tail coefficient (secular equation or characteristic polynomial) for **16** which can be quickly established with dense Sachs subgraphs.^[6] Thus, the PM3 results for the alternant system **16** are expected to provide the maximum symmetry allowed by its topology.

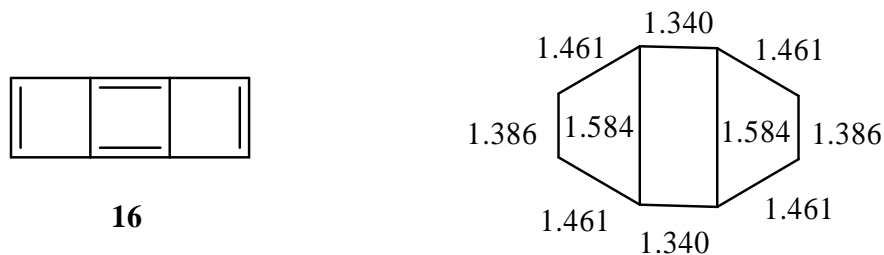


Fig. 17. A traditional Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state for tricyclo[4.2.0.0^{2,5}]octatetraene **16**.

The PM3 results conform to the expectations just outlined. Since **16** does not have a C_6 perimeter, there is no structural basis for anticipating π -bond delocalization. While one might be tempted to consider the notation shown in Fig. 18, it is precluded by the high symmetry expectation following from the tail coefficient for **16**.

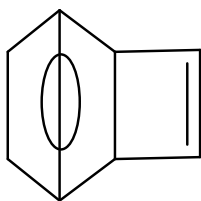


Fig. 18. A low-symmetry structure for tricyclo[4.2.0.0^{2,5}]octatetraene **16** which is inconsistent with both the Hückel level ($|a_n| \neq 0$) and PM3 computations for the lowest-lying singlet state.

Assuming (i) long ring junctures, as has been the case in every example heretofore, (ii) maximum symmetry for the topology ($|a_n| \neq 0$) and (iii) π -bond localization ($4N$ rings), there are still two possible π -bond dispositions (see competing possibilities in Fig. 19) for its $4N$ ($N = 2$) perimeter.

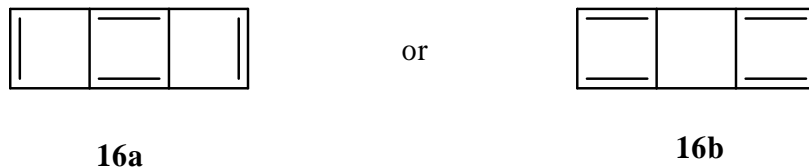


Fig. 19. Alternative, traditional Lewis structures for tricyclo[4.2.0.0^{2,5}]octatetraene **16**.

Once again, given that **16** is a small molecule, the choice can be made from the nodal properties of its HOMO which can be deduced from a partial correlation diagram. In this case, in contrast to the partial correlation diagram in Fig. 13, the work can be further simplified. The starting structure, [4]radialene, has HOMO/LUMO nodal properties that correspond to those for an acyclic polyene i.e. for the HOMO of **16**, nodes between each ethylene HOMO placed on the framework and for the LUMO of **16**, bonding interactions between each ethylene LUMO placed on the framework.^[1] Thus, the simplified construction of a partial correlation diagram (Fig. 20) for **16** leads to the unambiguous selection of **16a** as the proper Lewis structure in complete accord with the PM3 results (Fig. 17).

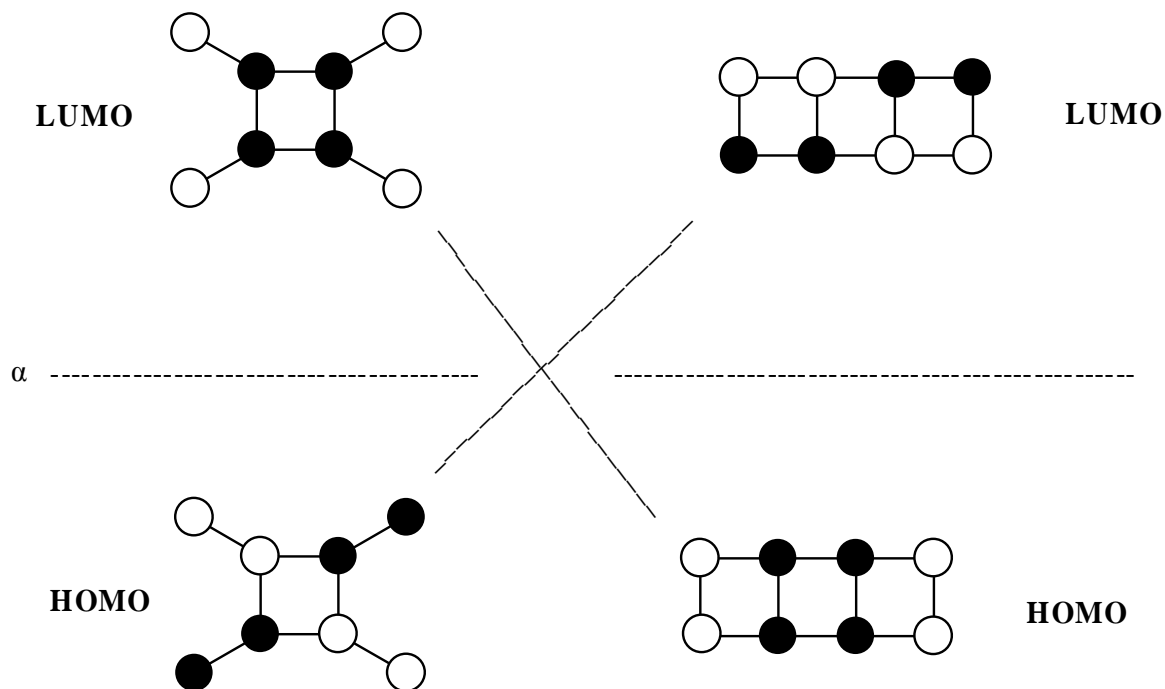


Fig. 20. A partial correlation diagram for the conversion of the [4]radialene π -system into the π -system of tricyclo[4.2.0.0^{2,5}]octatetraene **16**. This diagram leads to the conclusion that **16a** (Fig. 19) is the appropriate choice for **16**.

The preceding discussion of structures with $4N$ rings leads to a fascinating structural problem in which a conflict between structural expectations arises naturally. The linear polycycle, tetracyclo[4.4.0^{2,5}.0^{7,10}]decapentaene **17** has a pair of NBMOs ($|a_n| = 0$) at the Hückel level ($6N+4$ framework of carbon atoms^[9]). Alternatively, **17** can be embedded for an NBMO as shown in Fig. 21.

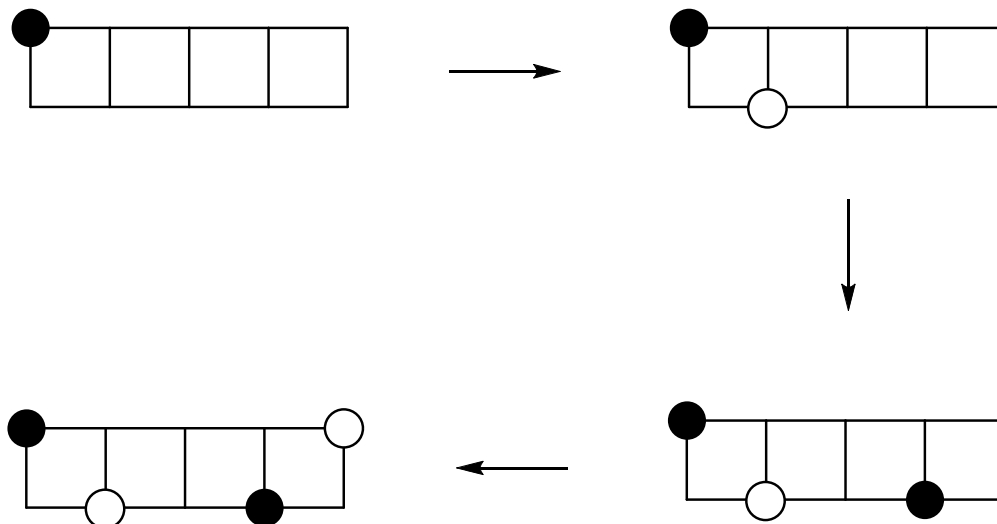


Fig. 21. Trial and error embedding for an NBMO on the skeleton of tetracyclo[4.4.0.0^{2,5}.0^{7,10}]decapentaene **17**. The procedure shows that alternant hydrocarbon **17** must have at least two NBMOs.

Like cyclobutadiene **15**, the tetracycle **17** is a Hückel triplet and should (Jahn-Teller) have the diminished symmetry that would accompany bond length alternation. On the other hand, from the vantage point of the current discussion, **17** has a $4N+2$ ($N = 2$) perimeter that can be subdivided into a pair of fused C_6 subperimeters, rather like those in naphthalene **5**. The optimized PM3 singlet structure for **17** provides a description that strongly supports the analogy to naphthalene **5** (see Fig. 22 and for comparison to **5**, see Fig. 23).

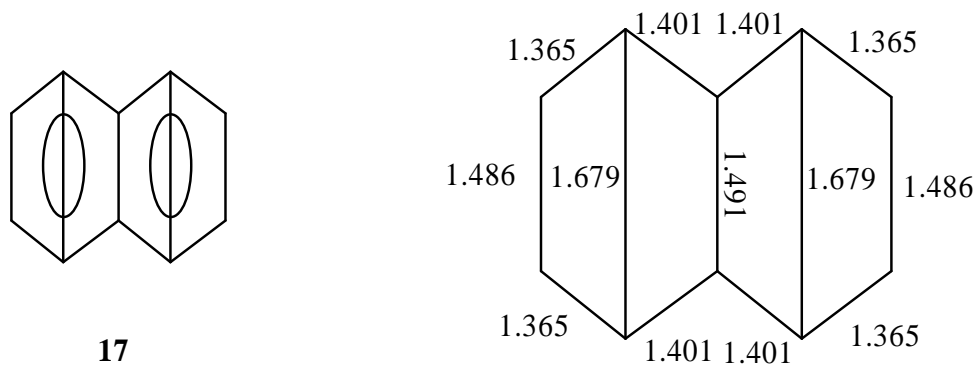


Fig. 22. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of tetracyclo[4.4.0.0^{2,5}.0^{7,10}]decapentaene **17**.

Relative CC Bond Lengths in Classical Fused Polycycles

Setting aside the long transannular bonds in tetracyclo[4.4.0.0^{2,5}.0^{7,10}]decapentaene **17** (Fig. 22), the similarity in the bond-length patterns between **17** and naphthalene **5** (Fig. 23) is striking.

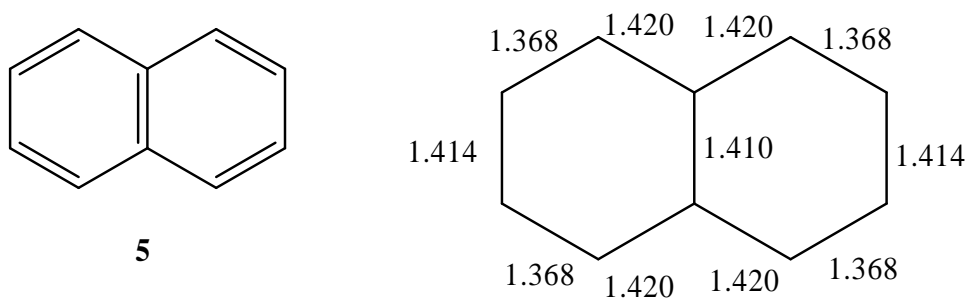


Fig. 23. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of naphthalene **5**.

The principal differences in the bond lengths for the ring juncture and the bonds opposite to it in naphthalene **5** and the corresponding bonds in **17** can be attributed to increased ring strain in **17** which leads to lengthening of its bonds. Note that within the structure of **5**, notwithstanding the relatively long ring juncture, the PM3 results match the Lewis structure given in Fig. 23 better than they match the specific π -bond placements in the other Kekulé contributors for **5**.

Now, consider benzocyclobutadiene **7** which has the trio of Kekulé contributors shown in Fig. 24.

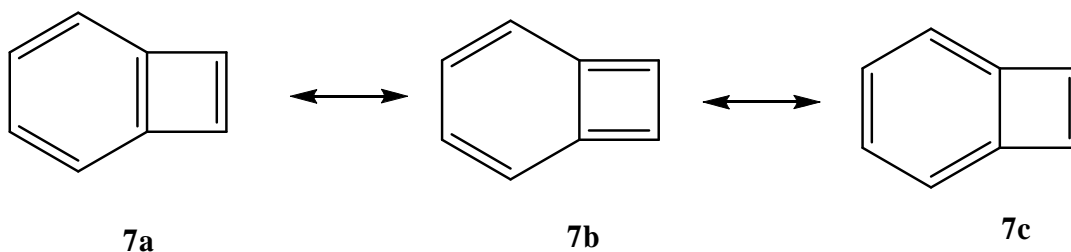


Fig. 24. Possible Kekulé contributors for the alternant hydrocarbon benzocyclobutadiene **7**.

PM3 calculations (Fig. 25) provided pronounced bond length alternation in a pattern, which for the C_6 elementary ring, is opposed to that found for either of the corresponding rings in naphthalene **5** (Fig. 23). That is, the best descriptor for **7** is **7c** in Fig. 24.

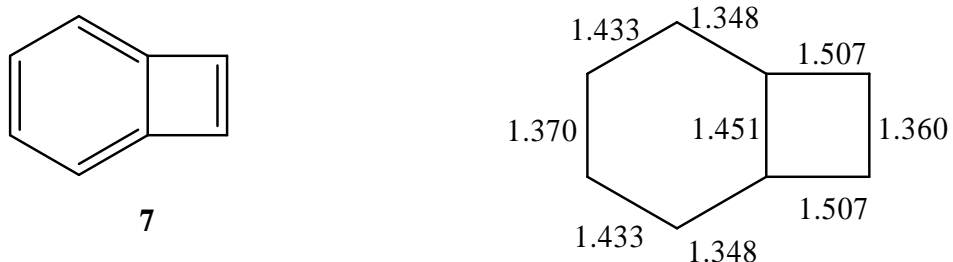


Fig. 25. A Lewis structure and PM3 calculated CC bond lengths for the lowest-lying singlet state of benzocyclobutadiene **7**.

With regard to the impact a fused ring has upon the π -bond placements of its neighbors, one could interpret the PM3 results in Figs. 23, 25 to mean that, for optimized lowest-lying singlet states, a C_6 elementary ring should have exclusively endocyclic π -bonds wherever possible and that a C_4 elementary ring should have at least two exocyclic π -bonds wherever possible.

If C_4 rings are energy minimized with the maximum number of exocyclic π -bonds, then the dimethano structure **18**, a relative of **7**, should have a PM3 optimized structure that matches **18a** rather than **18b** in Fig. 26.

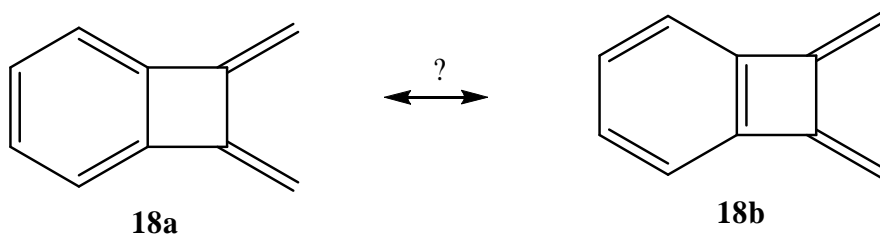


Fig. 26. Kekulé contributors for the dimethano benzocyclobutadiene **18**.

Note that **18** should have a PM3 description that features the maximum symmetry allowed by its topology ($|a_n| \neq 0$, quickly established using the edge deletion technique^[6]). Indeed, the PM3 description exhibits the expected symmetry and a Lewis structure that matches **18a** (see Fig. 27).

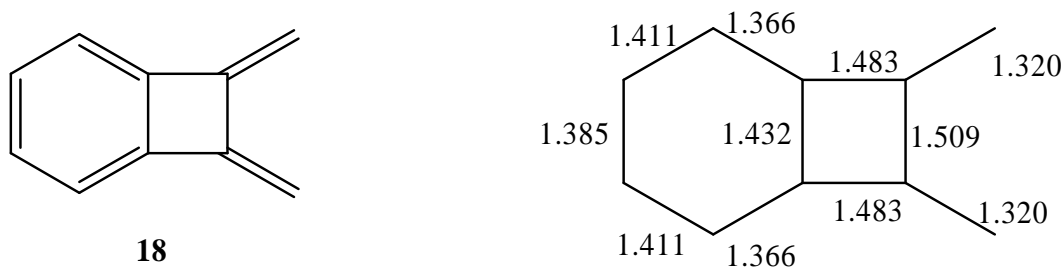


Fig. 27. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the dimethano benzocyclobutadiene **18**.

Further support for the contention that optimized PM3 structures have maximized the number of exocyclic double bonds for C_4 rings and have maximized the number of endocyclic double bonds for C_6 rings is evident from the PM3 results for biphenylene **19** (see Fig. 28).

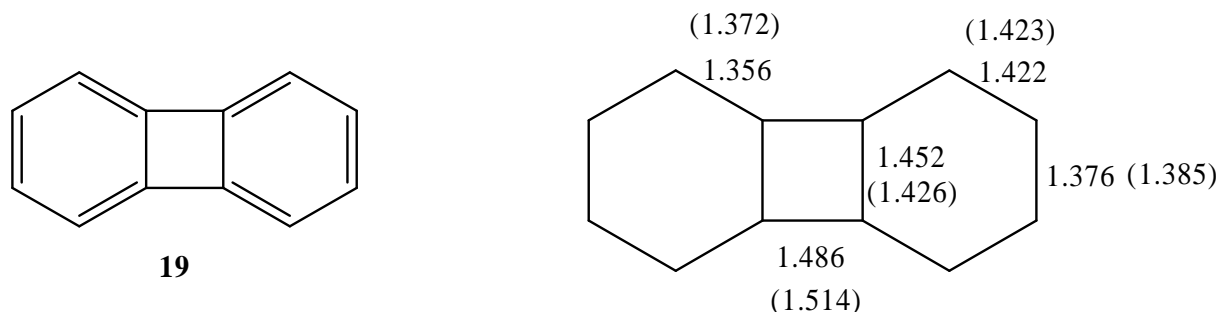


Fig. 28. A Lewis structure, PM3 calculated CC bond lengths (Å), and (in brackets) experimentally determined^[11, 12] bond lengths for biphenylene **19**. Biphenylene **19** should have a PM3 description showing the maximum symmetry allowed by its topology ($|a_n| = 9$, readily obtained using dense Sachs subgraphs.^[6])

A broader examination of PM3 results (more than two hundred structures) has led to the π -bond placement generalizations in Table 1 for $C_3 \rightarrow C_8$ rings.

Table 1. Semiempirical π bond placements for even, classical hydrocarbons

Given mandatory adherence to the Lewis octet rule in uncharged, even, classical hydrocarbon structures, the following preferences are found for PM3 optimized polycyclic structures.

Elementary Ring Size	Preferred π Bond Placement	Strong π Bond Localization?
3*	exocyclic	Yes
4*	exocyclic	Yes
5*	exocyclic	Yes
6	endocyclic	No
7	exocyclic	Yes
8	endocyclic	Yes

*Note the exceptional cases in which fused polycyclic perimeters provide a non-elementary C_6 circuit (see Figs. 14, 15 and 22).

A few structures will be used to adduce support for the generalizations in Table 1. Consider the Kekulé contributors for the non-alternant bicycle **20** (see Fig. 29).

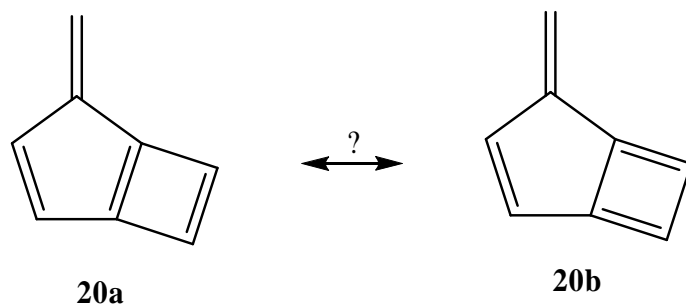


Fig. 29. Kekulé contributors for **20**.

Both the C₅ and the C₄ rings prefer π -bond localization (Table 1). The Lewis octet rule compels the C₄ ring to endure two endocyclic π -bonds. However the C₅ ring may have one (**20a**) or three (**20b**) exocyclic π -bonds. From Table 1, the energy minimized PM3 singlet state for **20** should and does match the expectation that corresponds to **20b** (see Fig. 30).

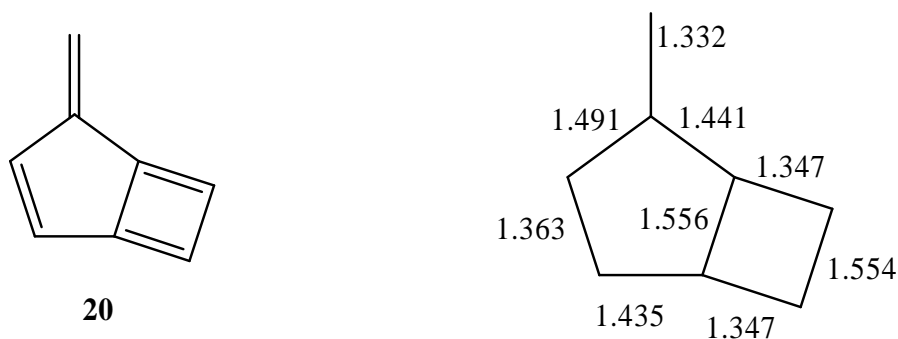


Fig. 30. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the non-alternant bicycle **20**.

The corresponding benzo-fused methylene cyclopentadiene system **21** makes an interesting structure for comparison with **20**. In this case, the C₅ and C₆ rings have opposed preferences for π -bond placement which can both be satisfied. The PM3 results for **21** are given in Fig. 31.

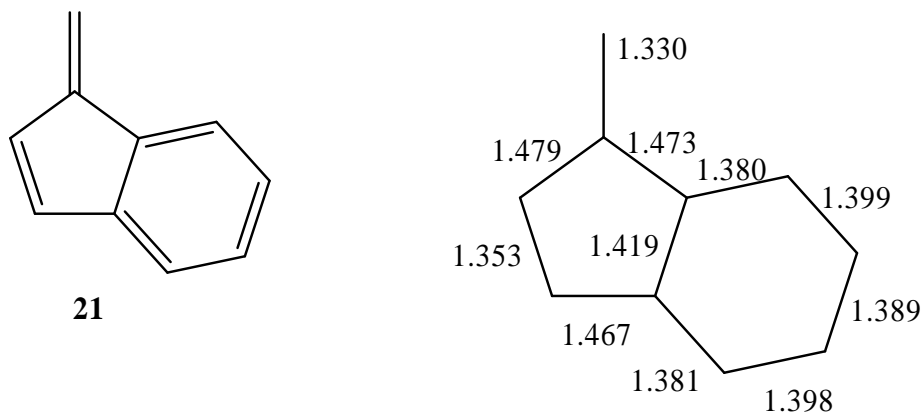


Fig. 31. The dominant Kekulé contributor and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the methylene cyclopentadiene **21**.

A comparison of the alternant rings in Figs. 30, 31 shows, not surprisingly (Table 1), that the C₄ ring (Fig. 30) has much more pronounced bond length alternation than PM3 predicts for the C₆ ring (Fig. 31). Nonetheless, it is clear from the bond lengths in Fig. 31 that the preferred Kekulé contributor for **21** would place a pair of endocyclic C₆ π-bonds so that they are exocyclic to the C₅ ring.

Smaller (especially C₃ and C₄) rings have a greater effect on PM3 calculated π-bond alternations than their larger relatives do. Compound **22**, in Figure 32, shows more pronounced π-bond localization than is exhibited in the results for **21** in Figure 31 (compare perimeters of the C₆ rings).

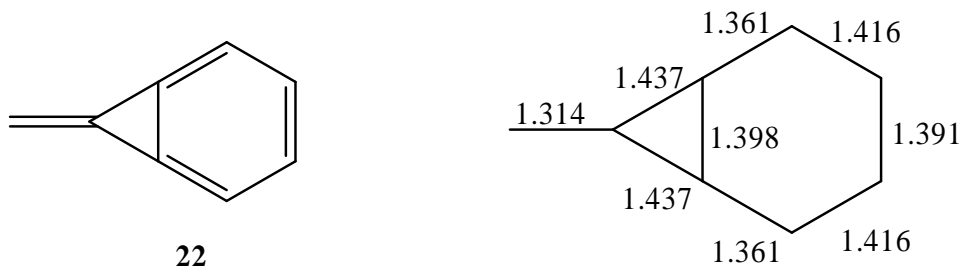


Fig. 32. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the methylene benzocyclopropane **22**.

As previously noted,^[2] the bond lengthening, of the ring juncture, associated with exocyclic placement of the second and third π -bonds (relative to the C_3 ring) leads to clearly diminished polarization of the structure.

A Simple Method to Recognize Preferred π -Bond Placements in Lewis Structures

Given the ideal π -bond placements shown in Table 1, π -bonding within each elementary ring may be characterized by noting the number of atoms in each elementary ring that do not participate in π -bonds of the preferred type versus the total number of atoms in that ring. This ratio will be called the Bond Placement Coefficient (B_{PC}).

The tetracycle **23** should have the maximum symmetry consistent with its topology ($|a_n| \neq 0$, readily deduced with the edge-deletion technique^[6]). Consider the Kekulé contributors for the tetracycle **23** (see Fig. 33).

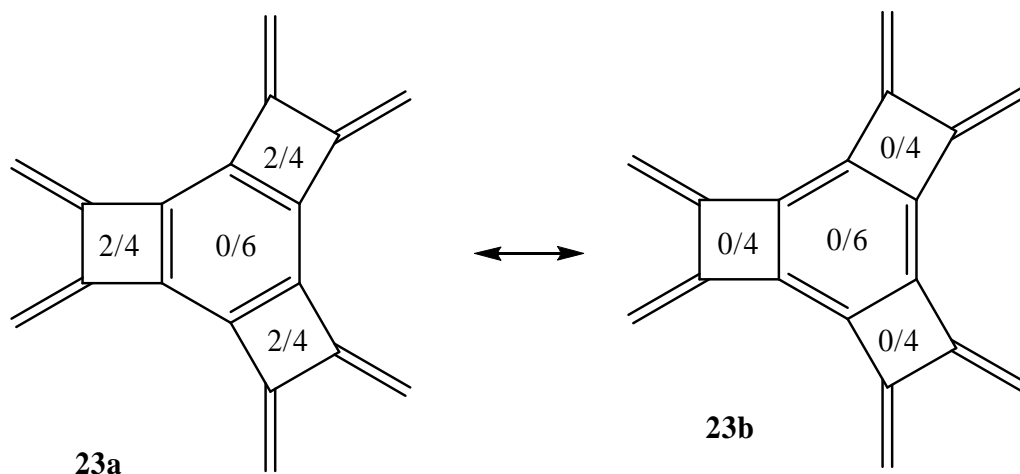


Fig. 33. Kekulé contributors for the tetracycle **23** showing the B_{PC} value for each elementary circuit.

Contributor **23a** features B_{PC} values of 2/4 for each C_4 elementary ring because two of the four carbons in each ring are involved in an undesirable endocyclic π -bond (Table 1). The C_6 ring has a B_{PC} value of 0/6 because none of its six carbons are involved in undesirable exocyclic π -bonds (Table 1). The superior contributor **23b** has the optimal B_{PC} values (general form 0/n where n is the number of carbons in the ring of interest). In general, it is particularly important to have minimal B_{PC} values for C_3 and C_4 rings, provided the Lewis octet rule has been satisfied. This analysis leads one to expect the PM3 results for the relative bond lengths which are given in Fig. 34.

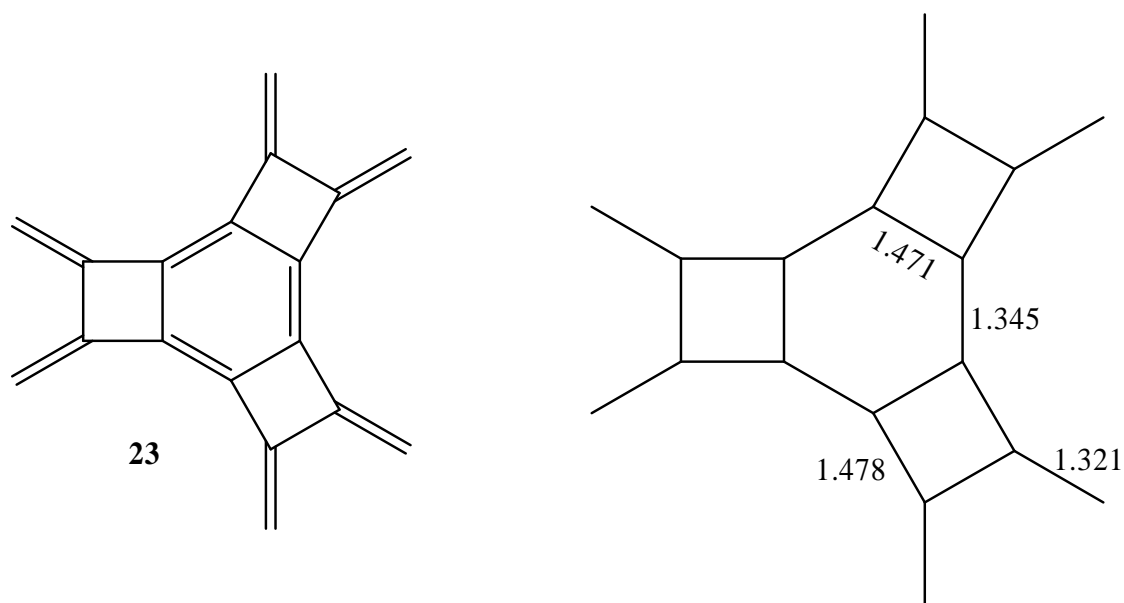
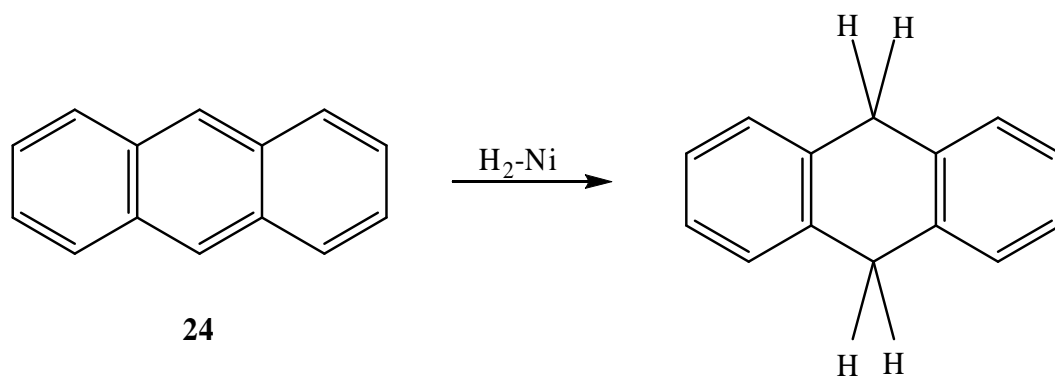


Fig. 34. A Lewis structure (features a C₃ axis) and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the tetracycle **23**.

Consider the well-known alternant hydrocarbon, anthracene **24**. In chemical reactions, it often gives products that arise by addition to the central ring (e.g. see Scheme 1).



Scheme 1.

Such results may be used to create the impression that the central ring has more pronounced π -bond localization (less aromatic) relative to the terminal rings. Evaluation of the appropriate Kekulé contributors by means of B_{PC} values is instructive (see Fig. 35).

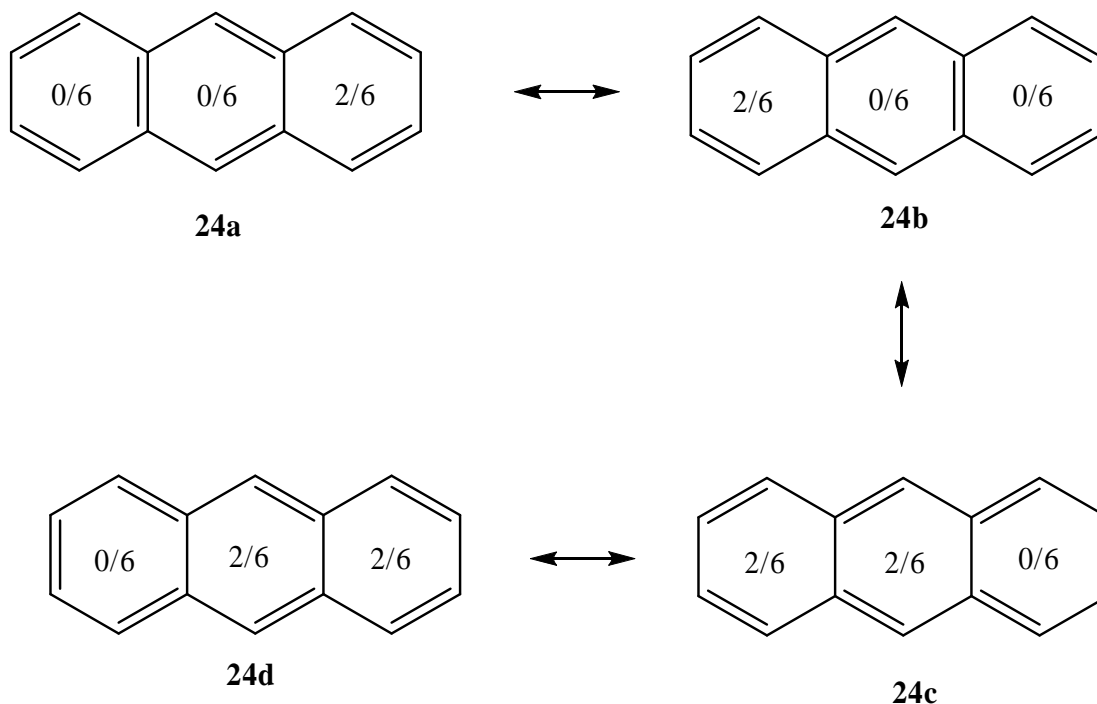


Fig. 35. Kekulé contributors for anthracene **24** showing the B_{PC} value for each elementary circuit.

From Fig. 35 it is clear that contributors **24a** and **24b** have the superior π -bond placements on account of having the smallest B_{PC} values. Hence, anthracene should have the poorest π -bond localization in the central ring. Based on contributors **24a** and **24b**, both the PM3 calculated and the experimentally-determined^[13] bond lengths are easily assimilated (see Fig. 36).

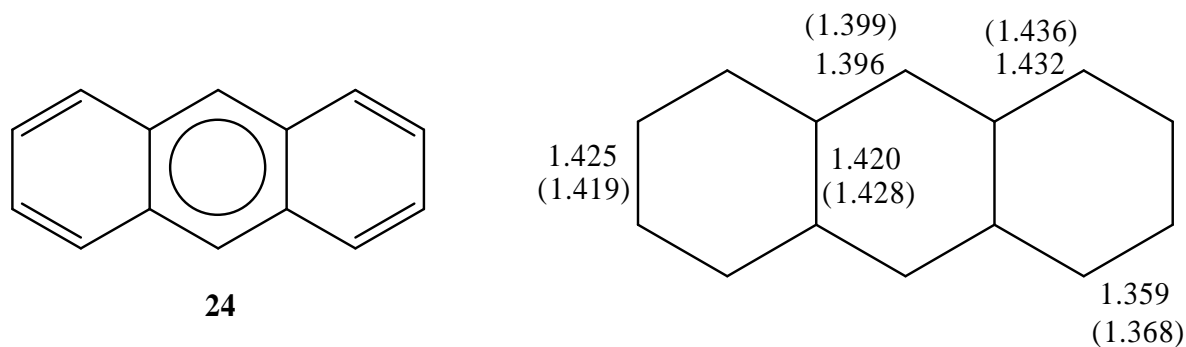


Fig. 36. A Lewis structure, PM3 calculated and (in brackets) experimentally determined CC bond lengths (Å) for the lowest-lying singlet state of anthracene **24**.

Relative ΔH_f Values (PM3 Calculated) for Selected sets of Polycycles

Given the preferred π -bond placements in Table 1, it should be possible to organize elementary rings in structural isomers, so that their placement preferences coincide or conflict. A case in point is provided by the naphthocyclobutadienes and biphenylene **19**.

Consider first, the Kekulé contributors for the conflicted naphthocyclobutadiene **25** (see Fig. 37).

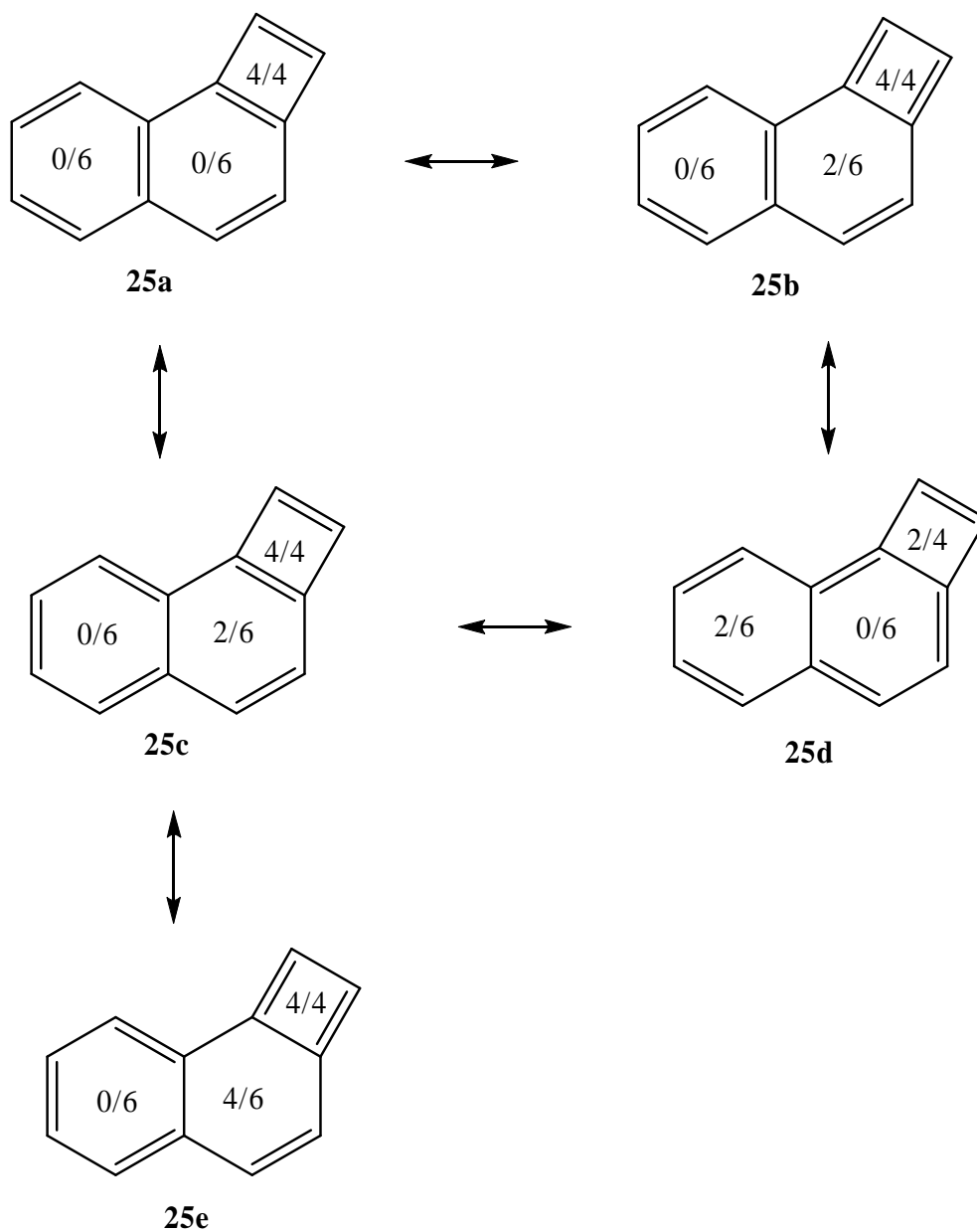


Fig. 37. Kekulé contributors for the tricyclic **25** showing the B_{PC} value for each elementary circuit.

From the B_{PC} values, one can infer that contributor **25e** is highest in energy, followed by the **25b**, **25c** pair and that the **25a**, **25d** pair are the lowest energy contributors. Given that the π -bond placement preferences of the C_4 ring are dominant, the PM3 calculated bond lengths should

largely conform to those implied by **25d**, as, indeed, they do (see Fig. 38).

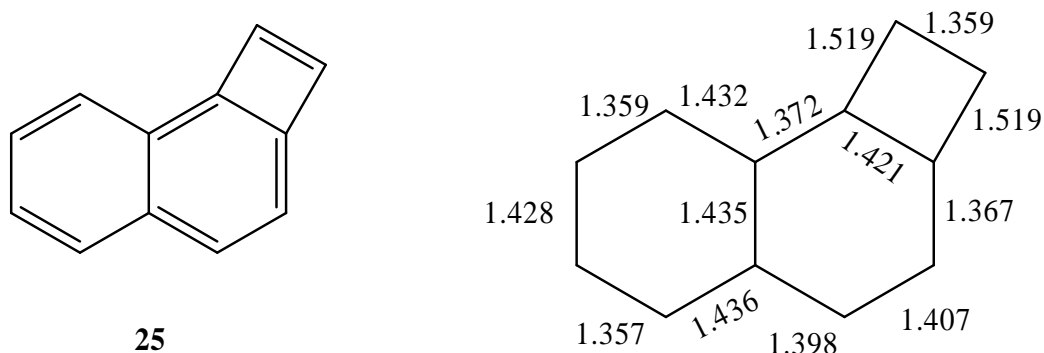


Fig. 38. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the naphthocyclobutadiene **25**.

In contrast to the conflicted naphthocyclobutadiene **25** for which the best descriptor has the B_{PC} values 2/6, 0/6, 2/4 (**25d**, Fig. 37), it is a simple exercise to find an internally unconflicted description for the naphthocyclobutadiene **26** (i.e. B_{PC} values of 0/6, 0/6, 2/4). Hence the PM3 description for **26** (Fig. 39) comes as no surprise.

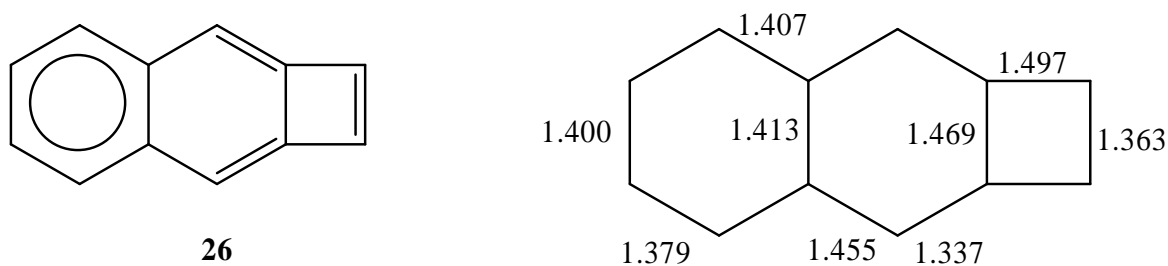


Fig. 39. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the naphthocyclobutadiene **26**.

Note that, at the Hückel level, **26** has $|a_n| = 4$ (deducible using dense Sachs subgraphs^[6])

so that the PM3 result should and does have a symmetry plane perpendicular to the molecular plane.

Biphenylene **19** (Fig. 28) has a Lewis structure for which the best descriptor has B_{PC} values of 0/6, 0/4, 0/6. Hence, for the isomers **19**, **25**, and **26** (each have a pair of fused C_6 rings and a fused C_4 ring), **25** has an unresolvable conflict between a C_6/C_4 pair, **26** has no internal conflict but has a C_4 ring that, as a consequence of the molecular topology, cannot reach the ideal B_{PC} value of 0/4 and **19** has an ideal set of B_{PC} values (general form 0/n). PM3 calculated enthalpies of formation have the order one would anticipate from the B_{PC} values: **25** (523.4 kJ/mol); **26** (481 kJ/mol); **19** (459.4 kJ/mol).

Consider the non-alternant fused bicycle **27**, in which the expected pronounced π -bond localization does not reduce molecular symmetry (see Fig. 40).

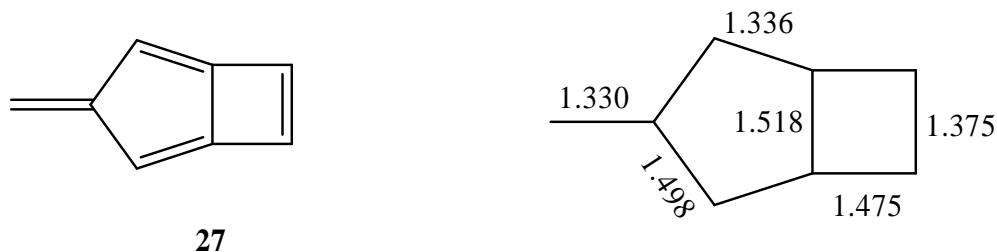


Fig. 40. A Lewis structure and PM3 calculated CC bond lengths (\AA) for the lowest-lying singlet state of the non-alternant bicycle **27**.

Although **27** (Fig. 40) is superior to its structural relative **20** (Fig. 30) (B_{PC} values: 4/5; 2/4 for **27** vs 2/5; 4/4 for **20**), each system has an unresolvable conflict between its rings i.e. neither structure can have B_{PC} values of 2/5; 2/4. Consequently, one might expect a particularly small difference between their PM3 calculated ΔH_f values. In fact, the $\Delta\Delta H_f$ value for this pair of compounds (68.3 kJ/mol) is greater than the largest $\Delta\Delta H_f$ value for any pair of molecules in the

tricyclic trio just discussed. The relatively large $\Delta\Delta H_f$ value for the **27**, **20** pair could have been anticipated by a closer examination of **20**. Traditional Hückel calculations ascribe a pair of singly occupied non-bonding MOs to **20** (see Fig. 41) which leads PM3 calculations to produce greater distortions, especially larger bond length alternations, in an attempt to minimize the optimized structure's energy.

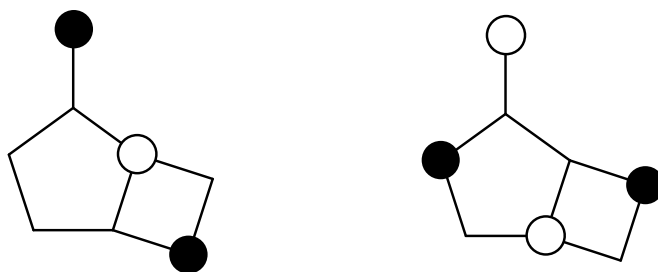


Fig. 41. Embeddable NBMOs for the non-alternant bicycle **20** (see also Fig. 30).

In the case of **27** and **20**, PM3 calculations produce a significantly longer ring juncture for **20** (Fig. 30, 1.556Å) than they do for **27** (Fig. 40, 1.518Å). Clearly, where relative energies are of interest, it is important to recognize even, classical hydrocarbons to which traditional Hückel calculations attribute NBMOs.

A more straightforward pair of structures (neither has an NBMO at the Hückel level which can be established using the edge-deletion technique^[6]) is provided by **22** (Fig. 32) and **28** (Fig. 42).

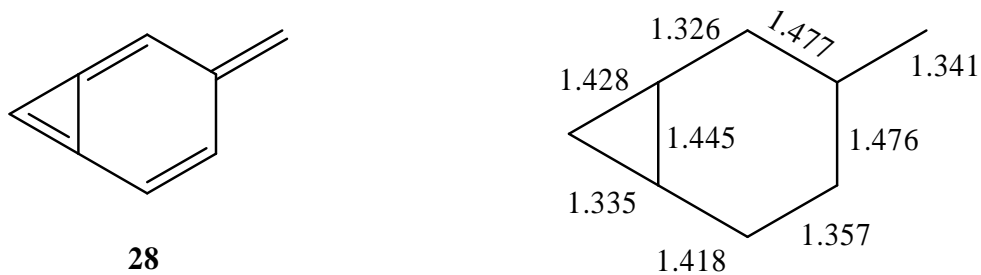


Fig. 42. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the non-alternant bicycle **28**.

Although both structures have a fused C_3/C_6 ring pair and an exocyclic methylene, **22** (unconflicted, B_{PC} values: 0/3, 0/6; PM3 calculated $\Delta H_f = 508.2$ kJ/mol) is readily recognized as the superior structure relative to **28** (conflicted, B_{PC} values: 2/3, 2/6; PM3 calculated $\Delta H_f = 598.7$ kJ/mol).

Structures **24** (Fig. 36) for anthracene and **6** (Fig 43) for phenanthrene constitute the final simple example, herein. They are a pair of alternant structures, each of which lacks an NBMO at the Hückel level (no $4N$ rings) so that each must have maximum symmetry for its topology.

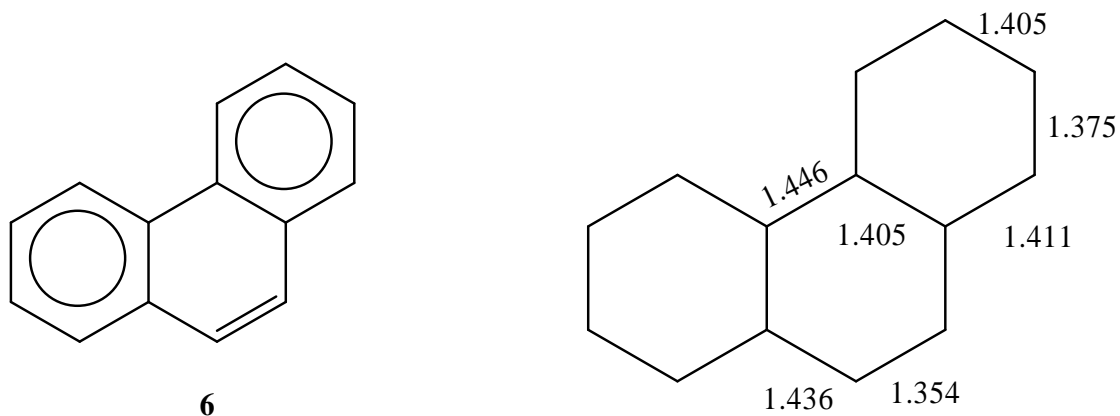


Fig. 43. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of phenanthrene **6**.

Not surprisingly, phenanthrene **6** (unconflicted, B_{PC} values: 0/6, 0/6, 0/6; PM3 calculated $\Delta H_f = 230.1$ kJ/mol) is the superior structure relative to anthracene **24** (conflicted, B_{PC} values: 0/6, 0/6, 2/6; PM3 calculated $\Delta H_f = 257.7$ kJ/mol).

Secondary Considerations: Elementary C_6 Rings

Aromatizing C_6 Rings Through Conflict in Polycycles

Classical hydrocarbon structures show stronger π -bond localization when there is no conflict between the optimal π -bond placements for each ring. The alternant compound **29** (maximum symmetry for its topology, apply edge deletion^[6] to see that $|a_n| = 4$) provides a nice example (see Fig. 44).

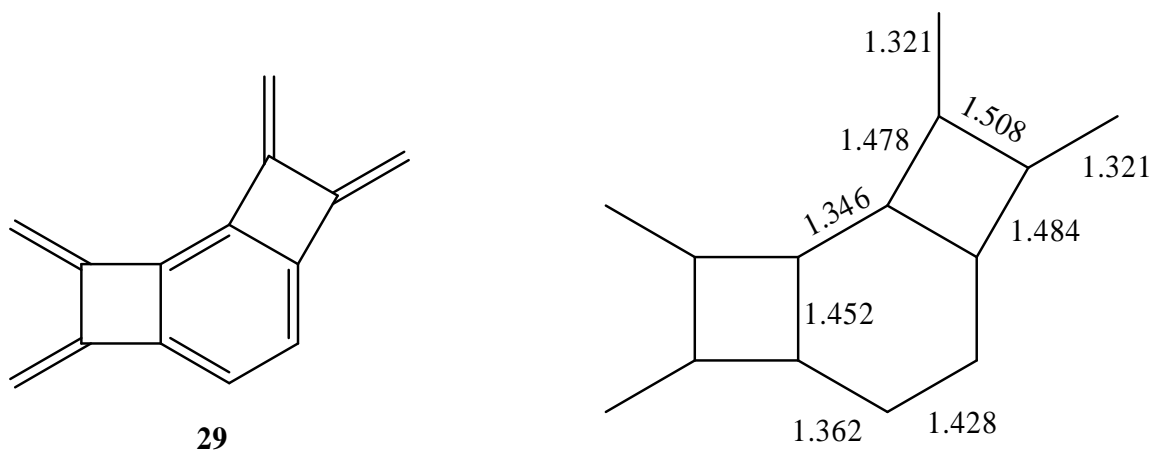


Fig. 44. A Lewis structure and PM3 calculated CC bond lengths (\AA) for the lowest-lying singlet state of the alternant tricycle **29**.

Note that the Lewis structure in Fig. 44 has B_{PC} values of 0/4, 0/6; 0/4 which are superior to those for the other Kekulé contributor (not shown) which has B_{PC} values of 2/4, 0/6; 2/4.

Structure **29** is closely-related to the tricycle, **30**, for which there is no disposition of the π -bonds that will satisfy both C_4 rings i.e. no descriptor has the B_{PC} values 0/4, 0/6, 0/4 (see Fig. 45).

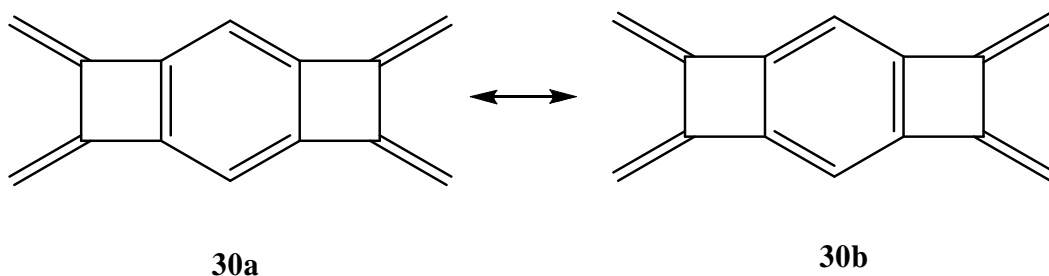


Fig. 45. Kekulé contributors for the alternant tricycle **30**.

At the Hückel level **30** has $|a_n| = 4$ (edge deletion^[6]) and should have a PM3 description featuring the maximum symmetry consistent with its topology. There is, however, insufficient molecular symmetry to enforce equal bond lengths around the subperimeter (associated with the C_6 ring). As a result the central ring resembles that shown in Fig. 14 for **4** (see Fig. 46).

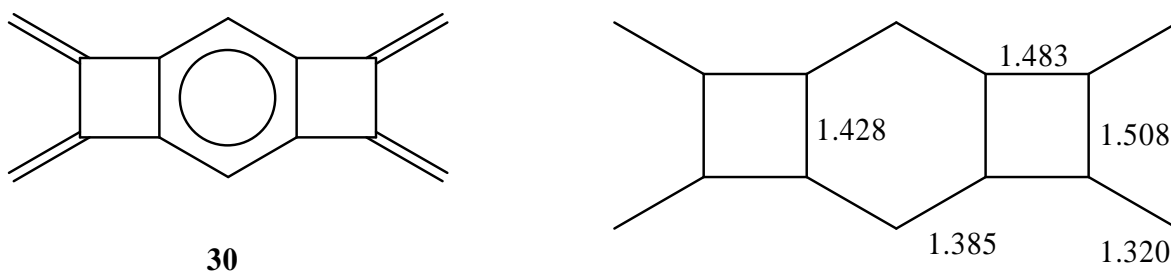


Fig. 46. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the tricycle **30**.

One might now expect that the unconflicted polycycle **29** would have a lower PM3 calculated ΔH_f value than that calculated for the conflicted polycycle **30**. But the conflicts in structure **30** have, as shown in the Fig. 46 Lewis structure, aromatized the central ring which enhances the stability (diminishes ΔH_f) and leads to very similar PM3 calculated enthalpies of formation for these two compounds: 730.1 kJ/mol for **29** (Fig. 44) and 725.9 kJ/mol for **30** (Fig. 46).

A contrasting pair of structures, in which the C₆ rings cannot be aromatized, show that the less conflicted structure does, as usual, have the smaller PM3 calculated ΔH_f value (see Fig. 47).

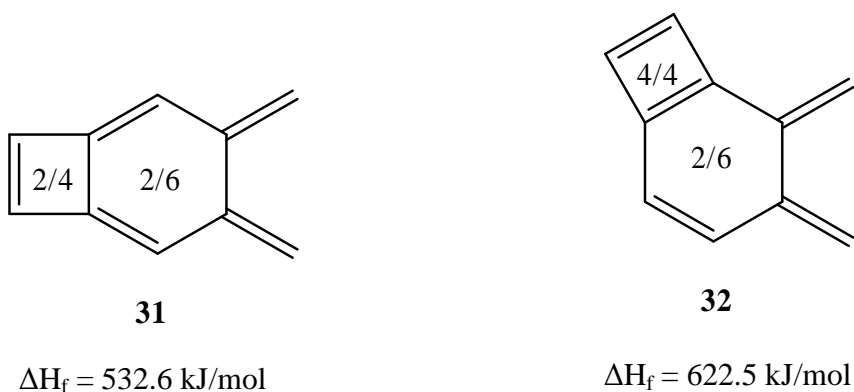


Fig. 47. Bicycle **31** has the lower ΔH_f because (i) it has a superior B_{PC} value for the C₄ circuit and (ii) **32** has pair of NBMOs at the Hückel level.

Note that the large $\Delta\Delta H_f$ for the **31**, **32** pair (Fig. 47) could be anticipated by recognizing that **32** is the more conflicted structure and that, at the Hückel level, it has a pair of NBMOs (to recognize that **32** has NBMOs (i) either embed for NBMOs or (ii) use edge deletion^[6]).

A particularly interesting problem is associated with compound **33**. Like **30** (Fig. 46), **33** features a conflicted pair of C₄ rings fused to an intervening C₆ ring (see Fig. 48).

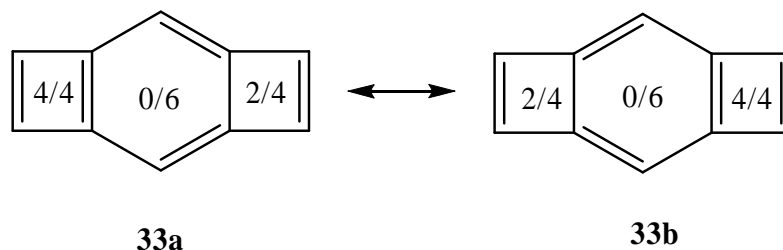


Fig. 48. Apparent aromatization of the central ring by means of π -bond placement conflict.

Once again, one might conclude that the internal conflict will lead to a PM3 description in which the central ring has been aromatized. However, in contrast to **30**, **33** has a pair of nonbonding Hückel eigenfunctions (see Fig. 49).

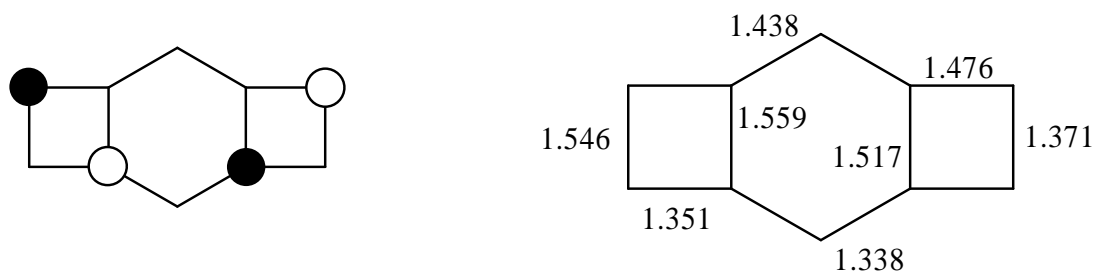


Fig. 49. One of two NBMOs showing that the alternant tricycle **33** is a Hückel triplet and PM3 calculated CC bond lengths (\AA) for the lowest-lying singlet state showing that resultant π -bond localization diminishes expected symmetry and precludes aromatization of the central ring (*cf* Fig. 48).

Thus, one expects greater distortion of the PM3 structure and clear peripheral bond length alternation.

The appropriate structural isomer of **33**, namely **34**, has no NBMOs, is less conflicted and, as a result, has the lower PM3 calculated ΔH_f value (see Fig. 50).

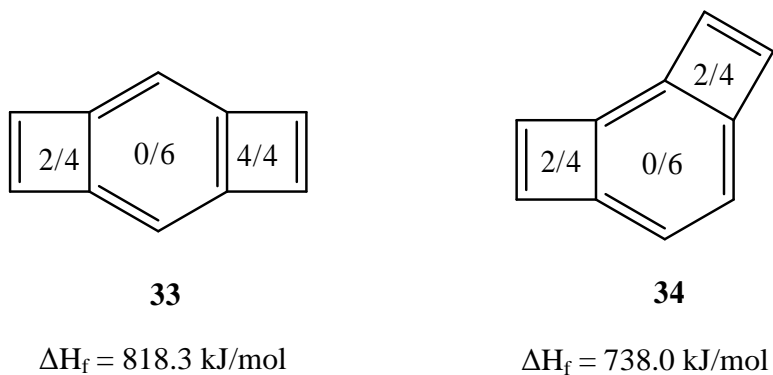


Fig. 50. PM3 calculated ΔH_f values for the lowest-lying singlet states of the conflicted Hückel triplet **33** and the unconflicted Hückel singlet **34**.

Preferred π -Bond Placement in Benzofused Non-alternant Hydrocarbons

Consider non-alternant hydrocarbons which (i) include a C₆ ring and (ii) have Kekulé contributors with identical sets of B_{PC} values. The non-alternant tricycle **35** (Fig. 51) will serve as the first example.

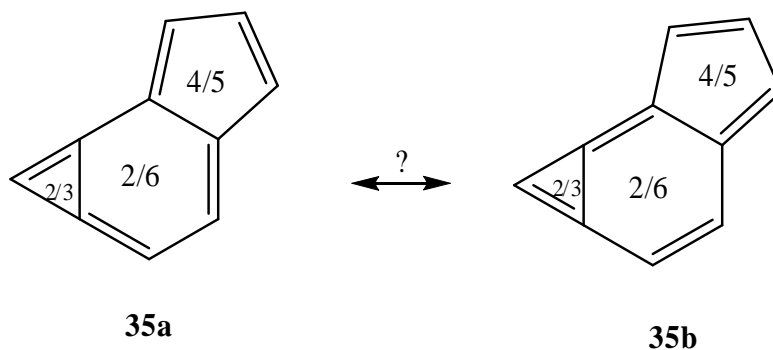


Fig. 51. Kekulé contributors for the non-alternant tricycle **35**.

Because **35** is non-alternant and the C₆ ring has no depiction that has B_{PC} = 0/6, one must choose between **35a** and **35b** which are structural alternatives rather than co-operating descriptors. In spite of having identical sets of B_{PC} values, **35a** and **35b** are not degenerate, thus the choice

between them requires some care. The salient difference between the alternatives arises in the central ring (see Fig. 52).

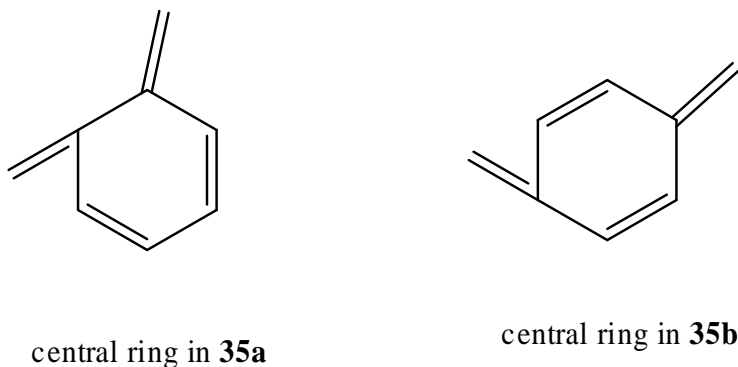


Fig. 52. π -Bond dispositions for the central rings in the Kekulé contributors for **35** (see Fig. 51).

When B_{PC} value sets are constant in structural alternatives for compounds like **35**, PM3 calculations consistently favor the “ortho” arrangement (**35a** in Fig. 51). Figure 53 presents the PM3 results for **35**.

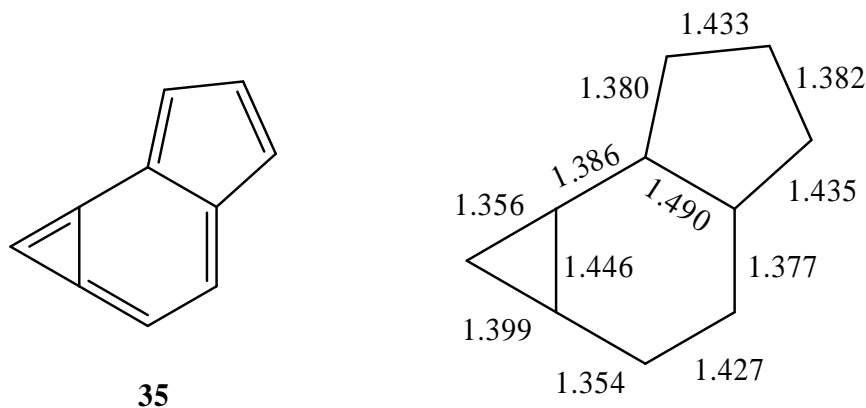


Fig. 53. A Lewis structure and PM3 calculated CC bond lengths (\AA) for the lowest-lying singlet state of the non-alternant tricyclic **35**.

Like **35**, the isomeric tricycle **36** (Fig. 54) has a pair of structural alternatives which share a common set of B_{PC} values.

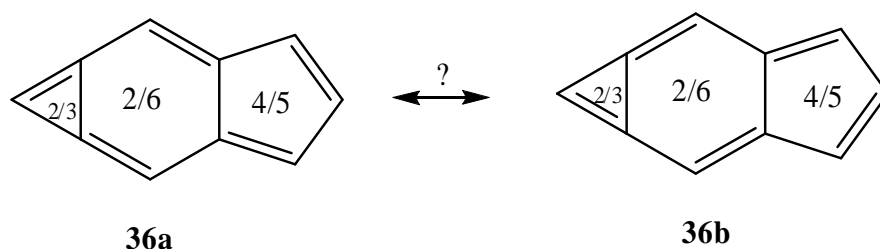


Fig. 54. Kekulé contributors for the non-alternant tricycle **36**.

Unlike **35**, **36** has degenerate structural alternatives so that either depiction (but not both) can be selected as the structure. The PM3 structural description (not shown) for **36** conforms to the expectations that accompany the choice of e.g. **36a** (Fig. 54) as the structure of **36**. Thus, in spite of the structures **35a** and **36a** sharing a common set of B_{PC} values, only **35a** has the superior ortho arrangement for the π -bonds in the C_6 ring. Hence, **35** is the superior isomer (see Fig. 55).

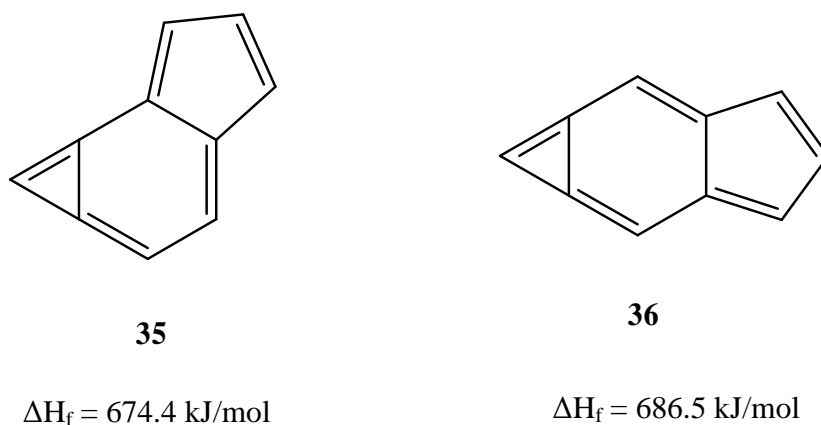


Fig. 55. Lewis structures and PM3 calculated ΔH_f values for the isomeric non-alternant tricycles **35** and **36**.

The preceding discussion leads to an informative consideration of another pair of non-alternant hydrocarbons. First consider the PM3 results for compound **37** (Fig. 56).

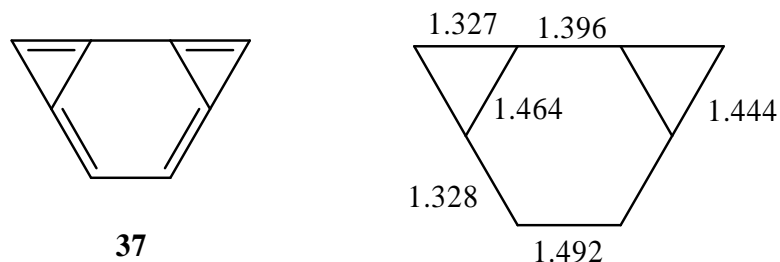


Fig. 56. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the non-alternant tricycle **37**.

Once again, the PM3 optimized structure **37** (B_{PC} values: $2/3$, $2/6$, $2/3$) has a pair of π -bonds arranged ortho to the C_6 ring.

Now consider the closely related isomer, **38** which has the Kekulé contributors shown in Fig. 57.

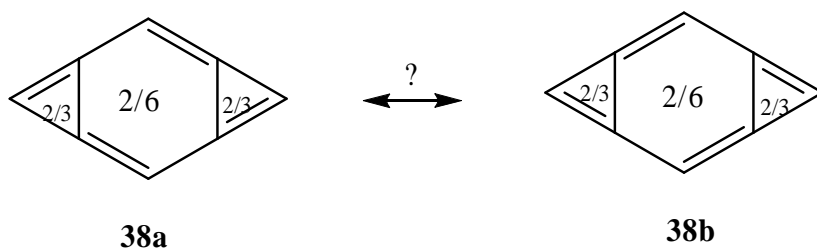


Fig. 57. Kekulé contributors for the non-alternant tricycle **38**.

Compound **38** is non-alternant, hence should have π -bond localization (choose one “contributor”, not both) and has identical sets of B_{PC} values for the degenerate “contributors” **38a**, **38b**.

Thus compound **37** has the modestly superior ortho arrangement, while **38** must have the modestly inferior para arrangement. What is worse for **38**, at the Hückel level, it is expected to

have an occupied NBMO (see Fig. 58), leading to the expectation of a PM3 description which has pronounced bond length alternation and substantial strain.

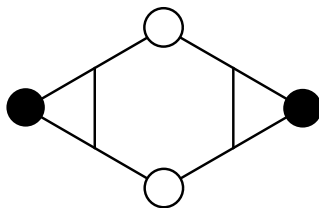


Fig. 58. An embeddable NBMO for the non-alternant tricycle **38**.

Perhaps, surprisingly, it is **38** that has the lower ΔH_f (see Fig. 59) and the $\Delta\Delta H_f$ value for the **37**, **38** structural pair is much larger than the $\Delta\Delta H_f$ value for the **35**, **36** structural pair (i.e. 54.4 kJ/mol vs 12.1 kJ/mol).

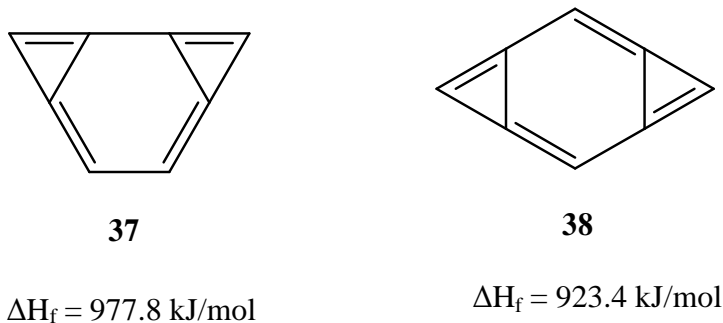


Fig. 59. PM3 calculated ΔH_f values for the isomeric tricycles **37** and **38**.

The solution to this apparent paradox can be found in an earlier discussion.^[14] From the graph-theoretical point of view, one can seek an imbalance (Δ) between the number of $4J+1$ and $4J+3$ circuits in the dominant Sachs' subgraphs for the non-zero characteristic polynomial coefficient closest to a_n . The difference in the numbers of such circuits (Δ) is equal to the difference in the

numbers of π -bonding and π -antibonding orbitals (at the Hückel level). Representative appropriate subgraphs are given in Fig. 60.

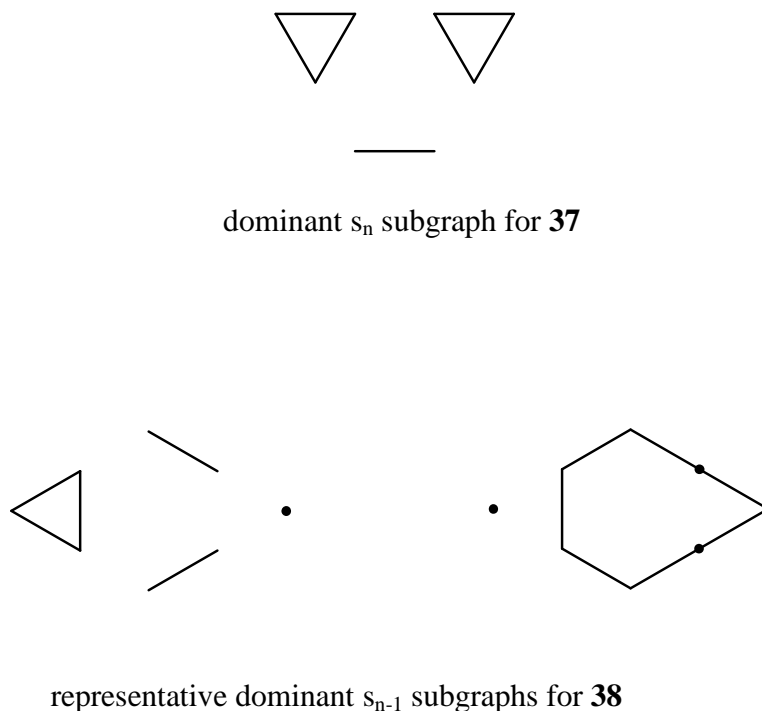


Fig. 60. Dominant Sachs subgraphs for the appropriate Characteristic Polynomial coefficients supporting the conclusions that (i) **37** has a doubly occupied antibonding orbital and (ii) **38** has a doubly occupied NBMO.

Since the dominant s_n subgraph for **37** (Fig. 60) features an excess of two $4J+3$ circuits ($\Delta=2$), the structure has two more antibonding orbitals (3 bonding, 5 antibonding) and so must have a doubly-occupied antibonding orbital. In contrast, the dominant s_{n-1} subgraphs for **38** (Fig. 60) feature an excess of one $4J+3$ circuit ($\Delta=1$) and the structure has one more antibonding orbital (3 bonding, 1 nonbonding, 4 antibonding) and so must have a doubly-occupied non-bonding orbital. These conclusions are depicted in Fig. 61.

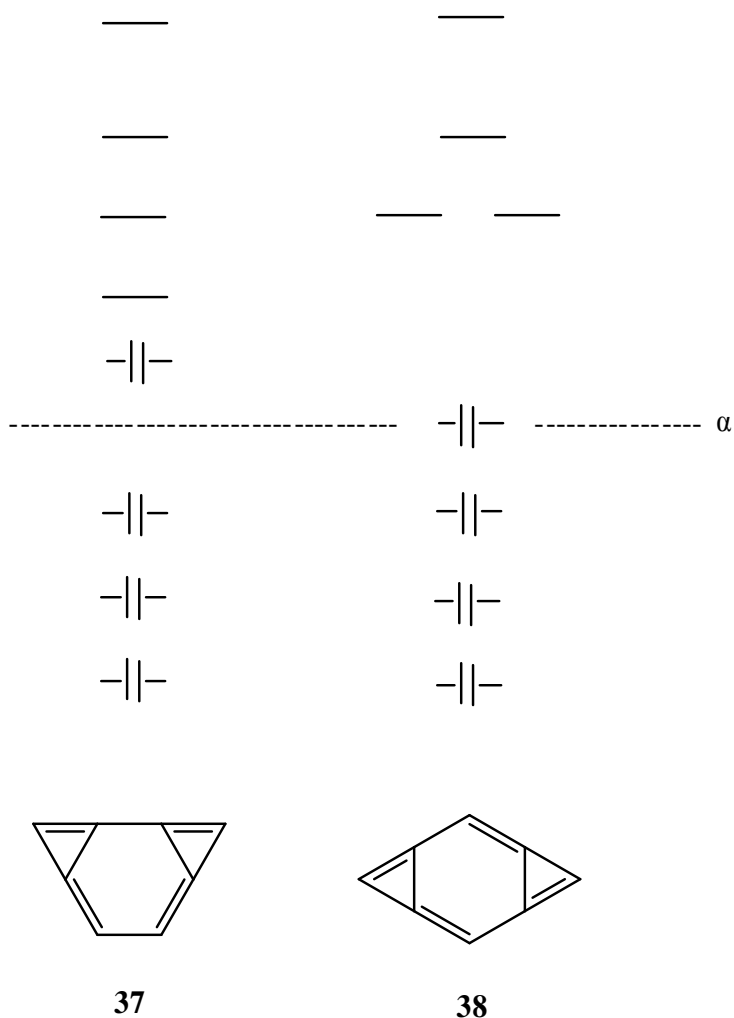


Fig. 61. π -Orbital occupancy (Hückel level) for the non-alternant tricycles **37** and **38**.

Clearly, **37**, although it lacks an NBMO, has the inferior arrangement for its π -electrons and should have the greater PM3 calculated distortions leading to the greater PM3 calculated ΔH_f (as shown in Fig. 59). Indeed, for the PM3 results on the **37**, **38** pair, **37** has the longer predicted ring junctures as well as the single longest bond in either structure (1.492Å in Fig. 56). PM3 results for **38** are shown in Fig. 62.

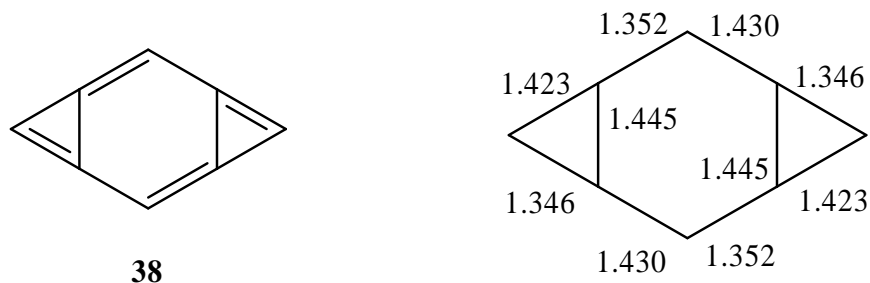


Fig. 62. A Lewis structure and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state for the non-alternant tricyclic **38**.

A parallel discussion can be offered for the non-alternant tricyclics presented in Fig. 63.

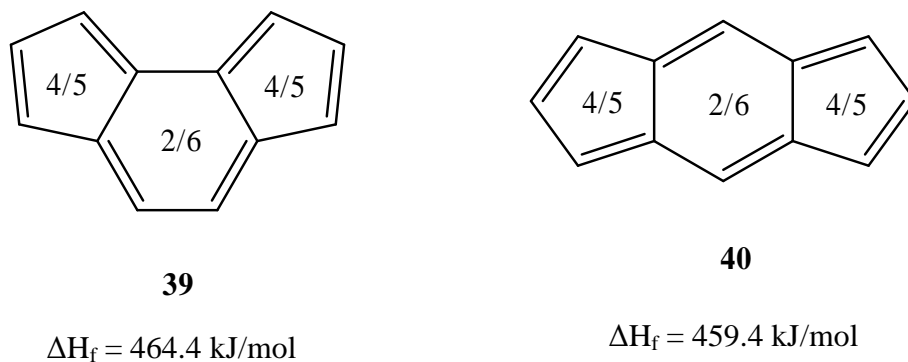


Fig. 63. PM3 calculated ΔH_f values for the non-alternant tricyclics **39** and **40**.

Once again, the structures have identical sets of B_{PC} values and the commonly superior “ortho” isomer (**39**) has the higher enthalpy of formation because it is a $\Delta=2$ structure as opposed to **40** which is a $\Delta=1$ structure. Representative, key subgraphs are provided for these structures in Fig. 64.

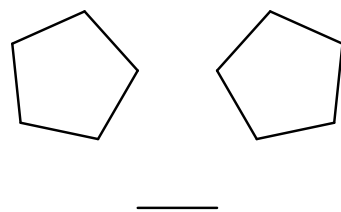
dominant s_n subgraph for **39**representative dominant s_{n-1} subgraphs for **40**

Fig. 64. Dominant Sachs subgraphs for the appropriate Characteristic Polynomial coefficients supporting the conclusions that (i) **39** has a vacant bonding orbital and (ii) **40** has a doubly occupied NBMO.

The major difference between the subgraphs in Fig. 60 and those in Fig. 64 is that the difference in non-alternant circuits in the Fig. 64 subgraphs refers to $4J+1$ circuits rather than $4J+3$ circuits. Hence, at the Hückel level, **39** has seven π -bonding orbitals and five π -antibonding orbitals and so must have a vacant bonding orbital rather than a doubly occupied antibonding orbital like **37**. As a result, the structural distortions for **39** are more modest and the PM3 calculated $\Delta\Delta H_f$ value for the **39**, **40** pair (5.0 kJ/mol) is much smaller than the corresponding number (54.4 kJ/mol) for the **37**, **38** pair (Fig. 59).

A final exemplary structural pair of $\Delta=0$ structures (Fig. 65) serves to offer further support for the contention that, given identical sets of B_{PC} values, the ortho isomer in appropriate sets of non-alternant hydrocarbons will have the lower enthalpy of formation.

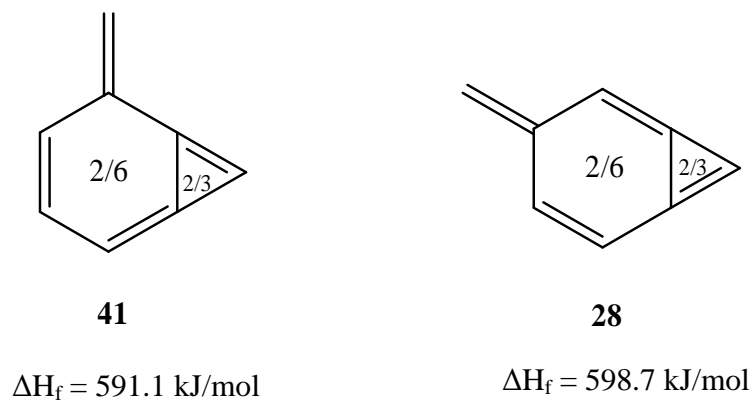


Fig. 65. PM3 calculated enthalpies of formation for **41** and **28**. Given a pair of isomers which have identical B_{PC} values, the lower ΔH_f is associated with the isomer which has the ortho disposition of π bonds.

Conclusions

Prior to the advent of systematically improved Hückel calculations, one needs to have a realistic view of relative bond lengths (long, short) for classical, even hydrocarbons. Table 1 provides explicit information about preferred π -bond placements for elementary rings ($C_3 \rightarrow C_8$) in such hydrocarbon structures. Those generalizations in conjunction with the newly-proposed parameters (B_{PC} values) provide a simple analytical scheme to assess the relative thermodynamic stabilities for closely-related polycycles. Predictions for exemplary sets of compounds have been checked by means of PM3 calculated bond lengths and ΔH_f values.

For closely related sets of structures which have identical B_{PC} values, routine analysis includes the secondary considerations (i) aromatized C_6 circuits arising from conflicts in preferred π -bond placements for different rings in the same structure and (ii) the preference in non-alternant structures PM3 calculations show for an ortho disposition of exocyclic π -bonds (relative to a C_6 ring) over a para arrangement (relative to a C_6 ring).

Traditional Hückel descriptions facilitate the process of anticipating PM3 results for those sets of structures which include a member that, at the Hückel level, (i) has one or more NBMO(s) or (ii) has an imbalance between the number of π -bonding and π -antibonding orbitals ($\Delta \neq 0$). These structures are subject to particularly large distortions and have particularly large ΔH_f values.

Chemical Graph Theory provides simple, powerful techniques for identifying such structures.

Traditional Hückel computations systematically provide structural descriptions of classical, even hydrocarbons that have the maximum symmetry permitted by their topology. Often when pronounced π -bond localization is incompatible with such high symmetry, PM3 descriptions lack that symmetry. Reduced symmetry arising from π -bond localization is a feature of PM3 descriptions of (i) non-alternant hydrocarbons and (ii) alternant structures containing $4N$ rings.

The use of Kekulé contributors in assessing such structures can be particularly troublesome.

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DFT CALCULATIONS ON SELECTED HYDROCARBONS

At the behest of a referee, a selection of hydrocarbon structures were subjected to DFT calculations to see whether B_{PC} predictions would stand up to such scrutiny. Five structures were selected – both the DFT and PM3 calculated bond lengths are given on the following pages. In no case did our expectations for relative bond lengths clash with DFT results.

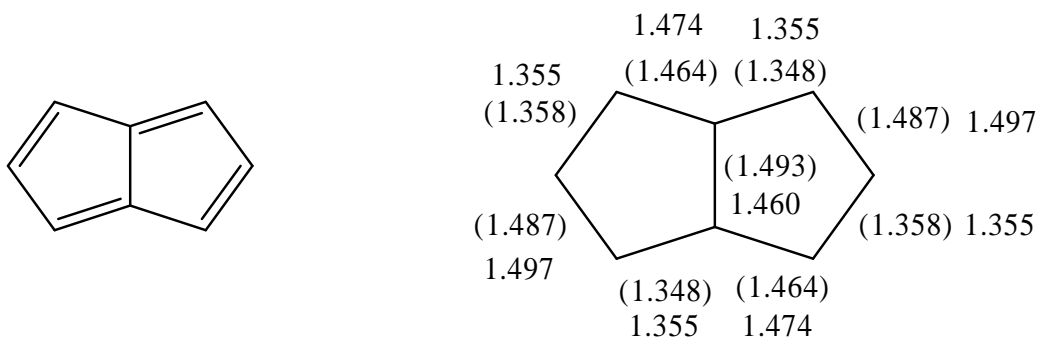
DFT results were kindly provided by Professor J. C. Baum of the Florida Institute of Technology.

B3LYP density functional theory calculations with the 6-31G* basis set were performed using Spartan '08 software. Complete geometry optimization with vibrational analysis resulted in planar structures.

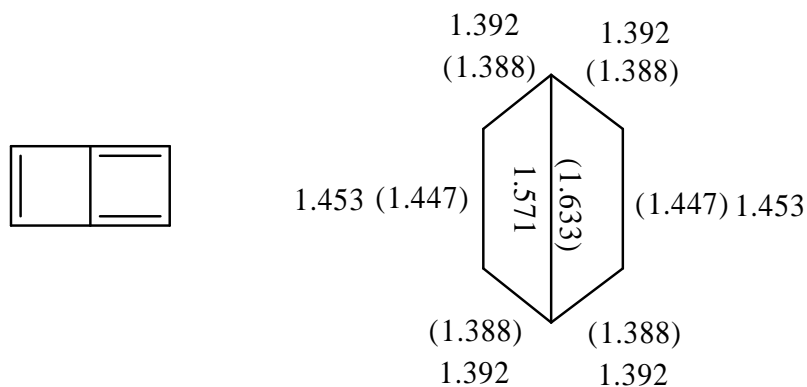
C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B Condens. Matter* **1988**, 37, 785.

A.D. Becke, *J. Phys. Chem.* **1993**, 98, 5648.

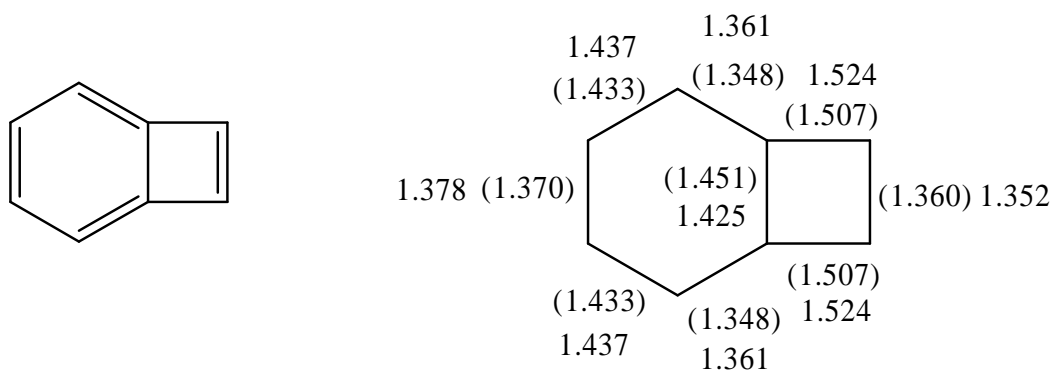
Spartan '08, Wavefunction, Inc.: Irvine, CA, USA



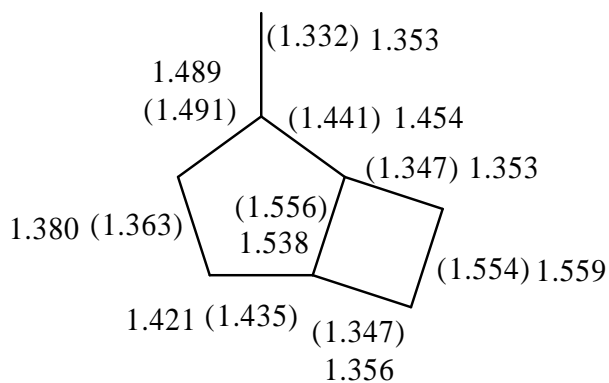
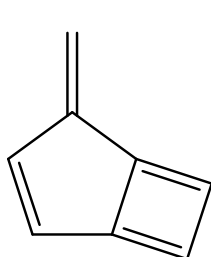
A Lewis structure, DFT calculated CC bond lengths (Å) and (in brackets) PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of pentalene.



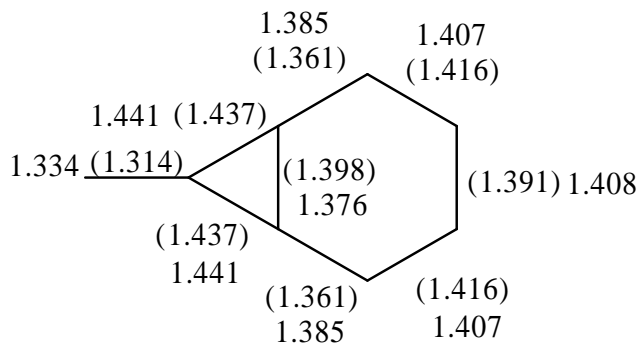
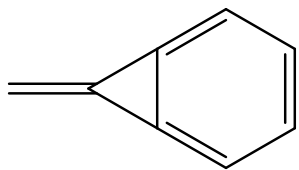
A Lewis structure, DFT calculated CC bond lengths and (in brackets) PM3 calculated CC bond lengths for the lowest-lying singlet state of bicyclo[2.2.0]hexatriene.



A Lewis structure, DFT calculated CC bond lengths and (in brackets) PM3 calculated CC bond lengths for the lowest-lying singlet state of benzocyclobutadiene.



A Lewis structure, DFT calculated CC bond lengths (Å) and (in brackets) PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of the non-alternant bicyclic molecule above.



A Lewis structure, DFT calculated CC bond lengths (Å) and PM3 calculated CC bond lengths (Å) for the lowest-lying singlet state of methylene benzocyclopropane.