

Why Are the Kinked Polyacenes More Stable than the Straight Ones? A Topological Study and Introduction of a New Topological Index of Aromaticity

Arkadiusz Ciesielski,^{*,†,‡} Tadeusz M. Krygowski,[‡] and Michał K. Cyrański[‡]

Institute of Biochemistry and Biophysics, Polish Academy of Science, Pawińskiego 5a, 02-106 Warsaw, Poland, and Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

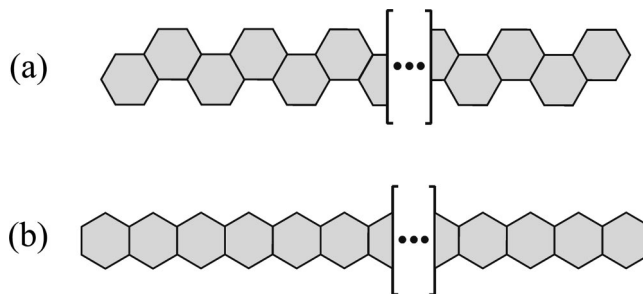
Received February 20, 2008

A topological model for estimating the stability of benzenoid hydrocarbons (BHs) is presented showing an acceptable linear dependence on Hess–Schaad resonance energy per π -electron values. The topological measure of stability is accessible by use of pencil calculation and is based on counting cis-type fragments of double bonds in all canonical structures of a given BH. Evidence is given that infinite chains of straight linear polyacenes are always less stable than the kinked ones.

INTRODUCTION

Phenanthrene and anthracene are both reactive in 9,10 positions, leading to products of addition.¹ However, from the very beginning, it has been recognized that phenanthrene is thermodynamically more stable than anthracene, with resonance energies, REs, equal to 110 and 105 kcal/mol, respectively.² Dewar and de Llano³ found REPE values (RE per π electron) equal to 0.138 and 0.114 eV, respectively, whereas Hess and Schaad⁴ found 0.055 and 0.047/ β (β is the Hückel molecular orbital unit of energy).⁵ In a recent review,⁶ a wide variety of RE values are reported, indicating always a greater stability of phenanthrene. This is observed despite potential steric interactions between hydrogen atoms in the 4 and 5 positions. In the case of *s-cis*- and *s-trans*-butadiene, the difference in energy is about 3 kcal/mol (depending on the level of calculation or experimental measurements),⁶ in favor of the trans conformer. Empirically, the phenomenon of a greater stability of phenanthrene was frequently explained by an old chemical idea, namely, that of two iso- π -electron systems: the one for which the number of canonical structures is greater is more stable.⁷ This is equivalent to application of the Clar rule,⁸ which states that phenanthrene may be described by a canonical structure with two Clar sextets, which stabilize the molecular system more effectively than one migrating sextet in the case of anthracene. The problem has been then tackled⁹ by several topological approaches, like Wiener,¹⁰ Szeged,¹¹ Padmakar–Ivan,¹² or Sudhana.¹³ The picture of phenanthrene enhanced stability has recently been discussed by Matta et al.¹⁴ on the basis of atoms in molecules theoretical analysis.¹⁵ They claimed to have stabilizing interactions between hydrogens in the C4 and C5 positions on the basis of the existence of a bond path between those two nuclei and the corresponding bond critical point. A very recent study by Bickelhaupt et al.¹⁶ has given a convincing argument that phenanthrene is more stable than anthracene because of more stabilizing interactions in the π -electron system, as follows

Scheme 1. The Kinked (a) and Straight (b) Benzenoid Hydrocarbons



Scheme 2. Canonical Structures of Naphthalene with Marked (Bold Lines) cis and trans Fragments



from the molecular orbital (MO) electronic structure analysis and quantitative bond energy decomposition in the framework of Kohn–Sham MO density functional theory.

The purpose of this report is to show that, by applying a topological approach, it is possible to find evidence that straight linear polyacenes are less stable than the kinked ones. Moreover, the evidence may also be derived for infinite chains of kinked (Scheme 1a) and straight (Scheme 1b) benzenoid hydrocarbons.

MOTIVATION AND METHODOLOGY

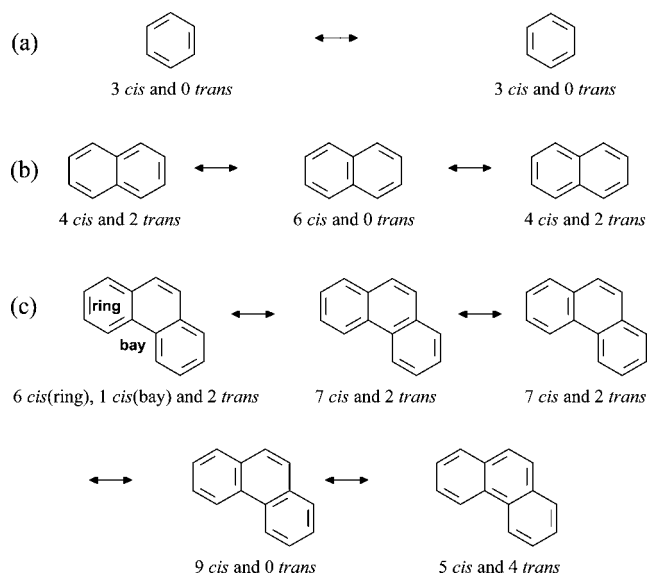
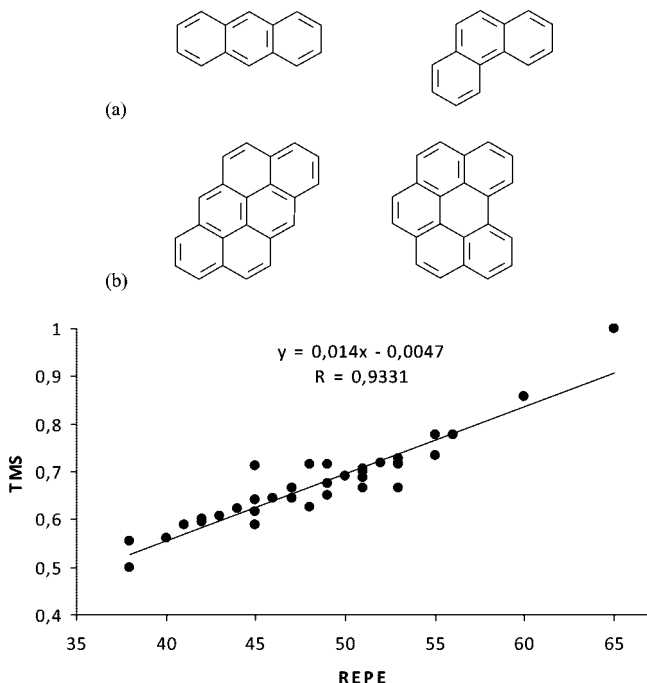
The idea of how to solve the above-presented problem is based on differentiation between two fragments of three sequential CC bonds, which may be recognized in the Kekule (canonical) structures of benzenoid hydrocarbons: one which may be named cis and the other named trans, as shown in Scheme 2.

The observation⁶ is that the role of each of these fragments in description of the whole molecule and its stability by use of canonical structures is different: the trans fragments destabilize the molecule of the benzenoid hydrocarbon, whereas the cis fragments are the stabilizing ones. This idea is close to that derived from the Randić theory of conjugated

* Corresponding author e-mail: arcad@ibb.waw.pl.

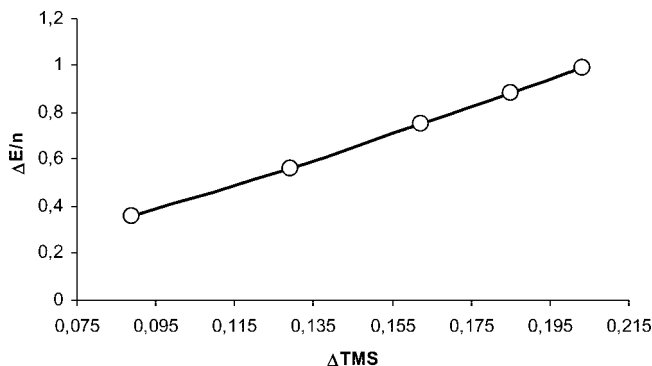
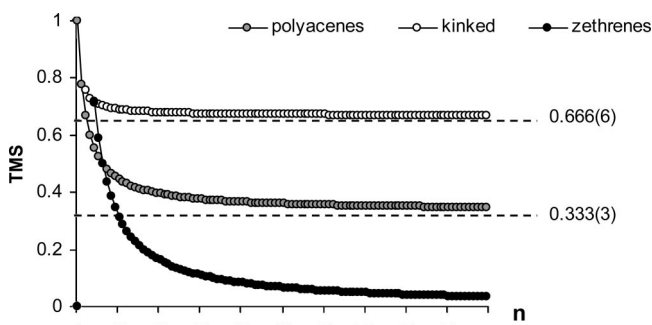
[†] Polish Academy of Science.

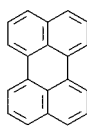
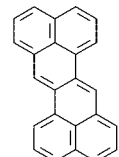
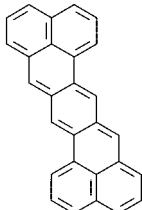
[‡] Warsaw University.

Scheme 3. Canonical Structures of Benzene (a) and Naphthalene (b) with the Number of cis, N_{cis} , and trans, N_{trans} , Fragments and (c) Two Different Kinds of cis Fragments: *cis*-(bay) and *cis*-(ring)**Scheme 4.** Two Pairs of Valence Isomers: (a) Anthracene and Phenanthrene and (b) Anthanthrene and Benzperylene**Figure 1.** Dependence of TMS values on Hess–Schaad REPEs for 40 benzenoid hydrocarbons. Correlation coefficient, $cc = 0.933$.

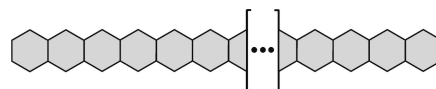
circuits.¹⁷ Following this theory, it can be stated that those benzenoid hydrocarbons which may be represented by a greater number of six-membered circuits and which contain only cis fragments, are more stable, that is, have greater REPE values. That is a reason why we have not included the cis fragment, which belongs to three rings in the so-called bay region. According to Randić theory, the contribution of conjugated circuits of this size is substantially lower than that of the six-membered ring.

The cases of benzene and naphthalene are convenient examples. In two canonical structures of benzene (Scheme 3a), there are altogether six cis fragments, whereas in the

**Figure 2.** Dependence of a difference between total energies per electron of kinked and straight benzenoid hydrocarbons, $\Delta E/n$, on ΔTMS for the first five pairs. The correlation coefficient is 0.9993.**Figure 3.** Dependences of TMS on the number of rings n in straight polyacenes, kinked polyacenes, and zethrenes.**Table 1.** Schemes of the First Three Representatives of Zethrene-Type Compounds^a

			
K	9	9	9
N_{cis}	90	90	90
$N_{trans} + N_{cis}$	126	153	180
TMS	0.714	0.588	0.500

^a For all of them are given the number of Kekule structures, K , the number of cis fragments, N_{cis} , and the total number of cis and trans fragments, $N_{trans} + N_{cis}$ and the value of TMS.

Chart 1

case of naphthalene for three canonical structures (see Scheme 3b), there may be found 14 cis-type fragments and four trans ones.

The REPE values, being intensive measures of stability, show that naphthalene is less stable than benzene.^{3,6} In such a situation, it seems reasonable to associate the stability of these molecules with the number of cis and trans fragments

Chart 2

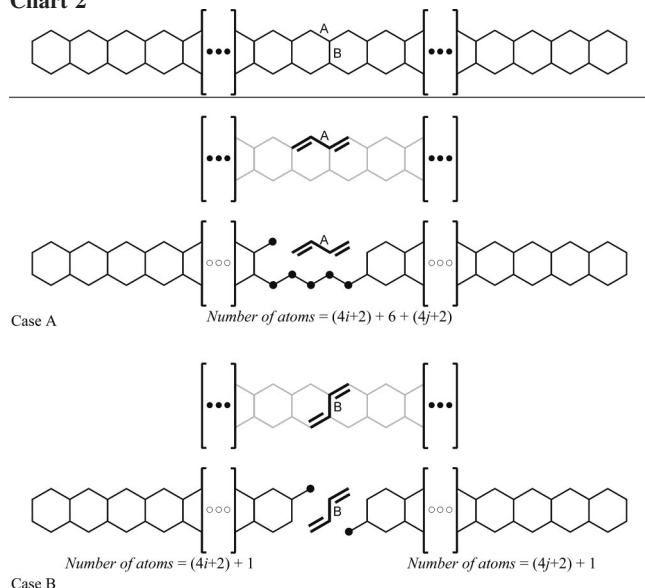
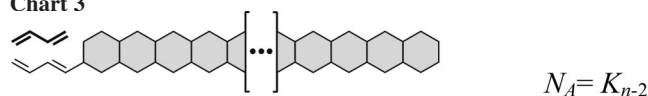


Chart 3



appearing in all canonical structures. Thus, we assume as a topological measure of stability (TMS) a quantity defined as the number of cis fragments, $N_{\text{cis}}^{\text{ring}}$, divided by the sum of N_{cis} and N_{trans} calculated for all canonical structures of a given molecule:

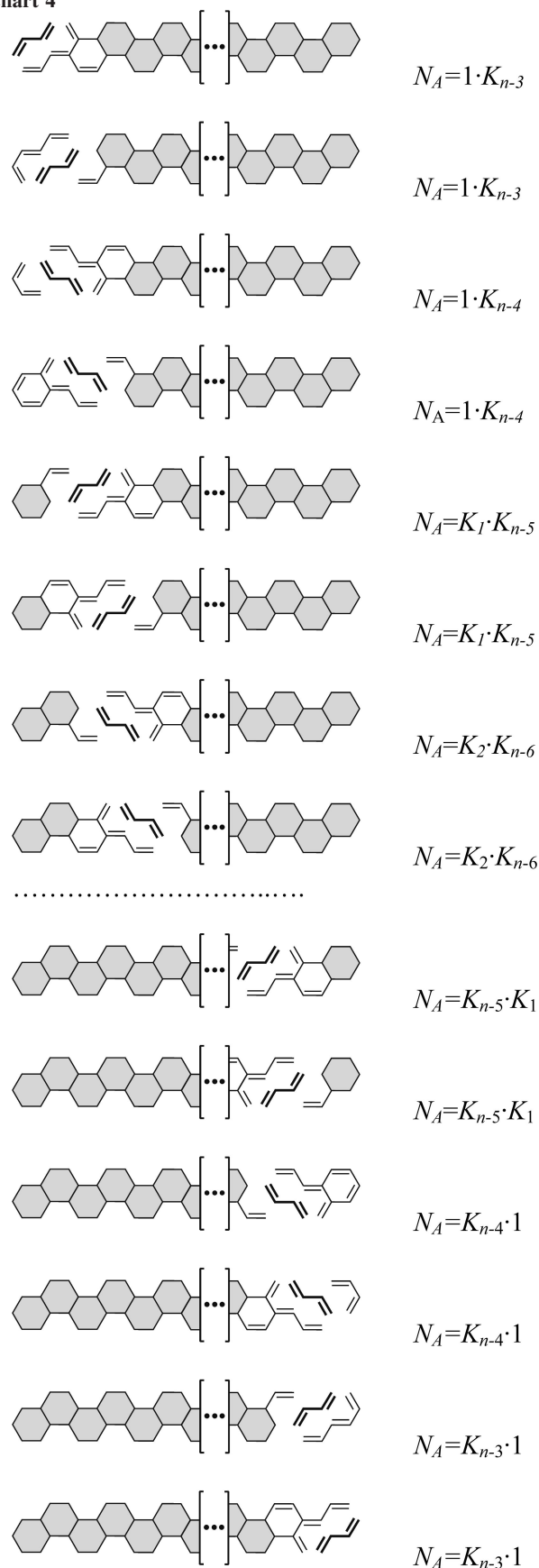
$$\text{TMS} = \frac{N_{\text{cis}}^{\text{ring}}}{N_{\text{cis}} + N_{\text{trans}}} = \frac{N_{\text{cis}} - N_{\text{cis}}^{\text{bay}}}{N_{\text{cis}} + N_{\text{trans}}} \quad (1)$$

Note that trans fragments may be realized only in two vicinal rings, whereas cis fragments may be realized either in one ring or in the so-called bay region (see the case of phenanthrene in Scheme 3c), *cis(bay)*. In formula 1, $N_{\text{cis}} = N_{\text{cis}}^{\text{ring}} + N_{\text{cis}}^{\text{bay}}$. It is important to say that the sum of cis and trans fragments in all canonical structures is equal to the number of canonical structures multiplied by the number of single bonds. Hence, it suffices to take into counting either cis or trans fragments.

For benzene and naphthalene, TMS values are $6/6 = 1.00$ and $14/18 = 0.77(7)$, respectively, which is in line with their stabilities. Additional encouraging results come from using TMS for pairs of valence isomers: (a) anthracene and phenanthrene and (b) anthanthrene and benzperylene (Scheme 4).

Anthracene and phenanthrene are the shortest representatives of the straight and kinked linear benzenoid hydrocarbons. The latter system is more stable by 5.0 kcal/mol (at B3LYP/6-311G**). The TMS values for these two systems are 0.66(6) and 0.75(5), which are in line with the sequence given by energies. Interestingly, for the other two molecules, which are in some way analogous to the linear and kinked ones, that is, anthanthrene and benzperylene, the difference in stability is 5.7 kcal/mol (at B3LYP/6-311G**), again indicating a greater stability of the “kinked” hydrocarbon, that is, benzperylene. The TMS values are again in line with this sequence and amount to 0.588 and 0.705, respectively.

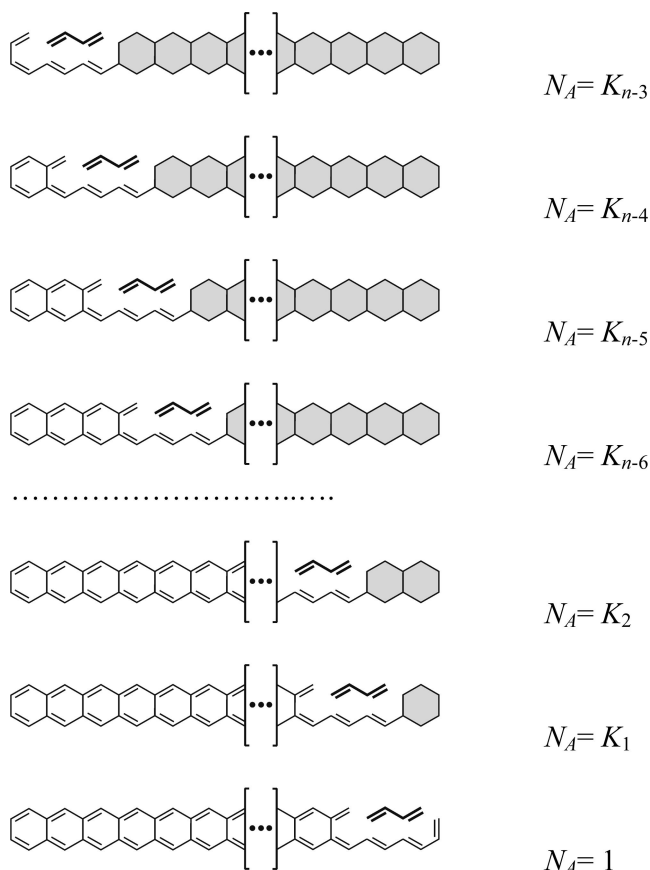
Chart 4



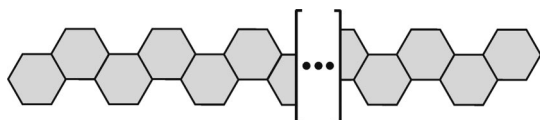
RESULTS AND DISCUSSION

The above conceptual reasoning needs support based on a greater set of data. To check the credibility of using TMS values as an intensive descriptor of stability, Figure 1 shows

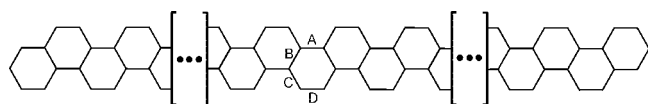
Scheme 5



Scheme 6



Scheme 7

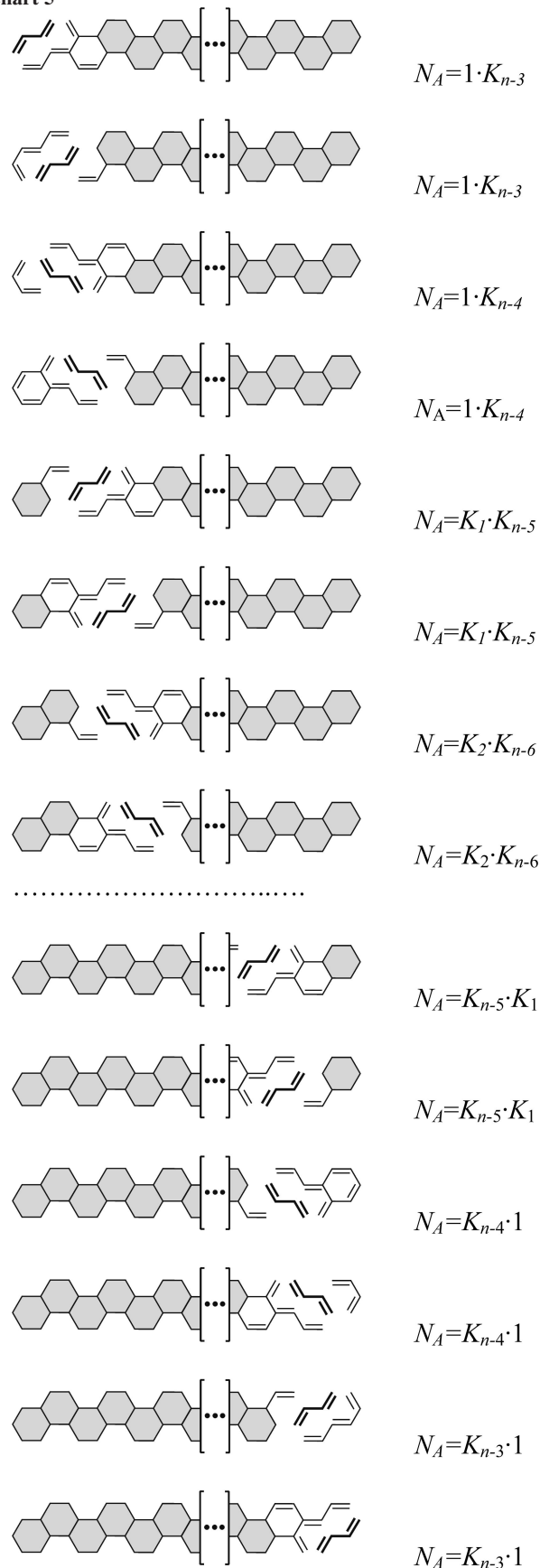


a dependence of TMS on the REPE values of Hess and Schaad for all hydrocarbons considered in their paper.⁴ A qualitative agreement is at least satisfactory—taking into account completely different theoretical bases for these two approaches. It is apparent that the rule is that, the greater value of TMS, the greater is REPE and the more stable thermodynamically is the system in question. In respect of this finding, TMS may be considered approximately as an energy-based index of global aromaticity of a given molecule of benzenoid hydrocarbon.

In order to approach the title problem, Figure 2 presents the dependence of a difference between total energies per electron of kinked and straight benzenoid hydrocarbons, ΔE , per electron, on ΔTMS for a few representatives of linear and kinked benzenoid hydrocarbons (data taken from ref 18 computed at the B3LYP/6-311G** level of theory). It should be mentioned here that less accurate $\Delta REPE$ values gave a similar picture for nine pairs of benzenoid hydrocarbons.⁴

The TMS values may be calculated not only for any particular straight or kinked benzenoid hydrocarbon but also

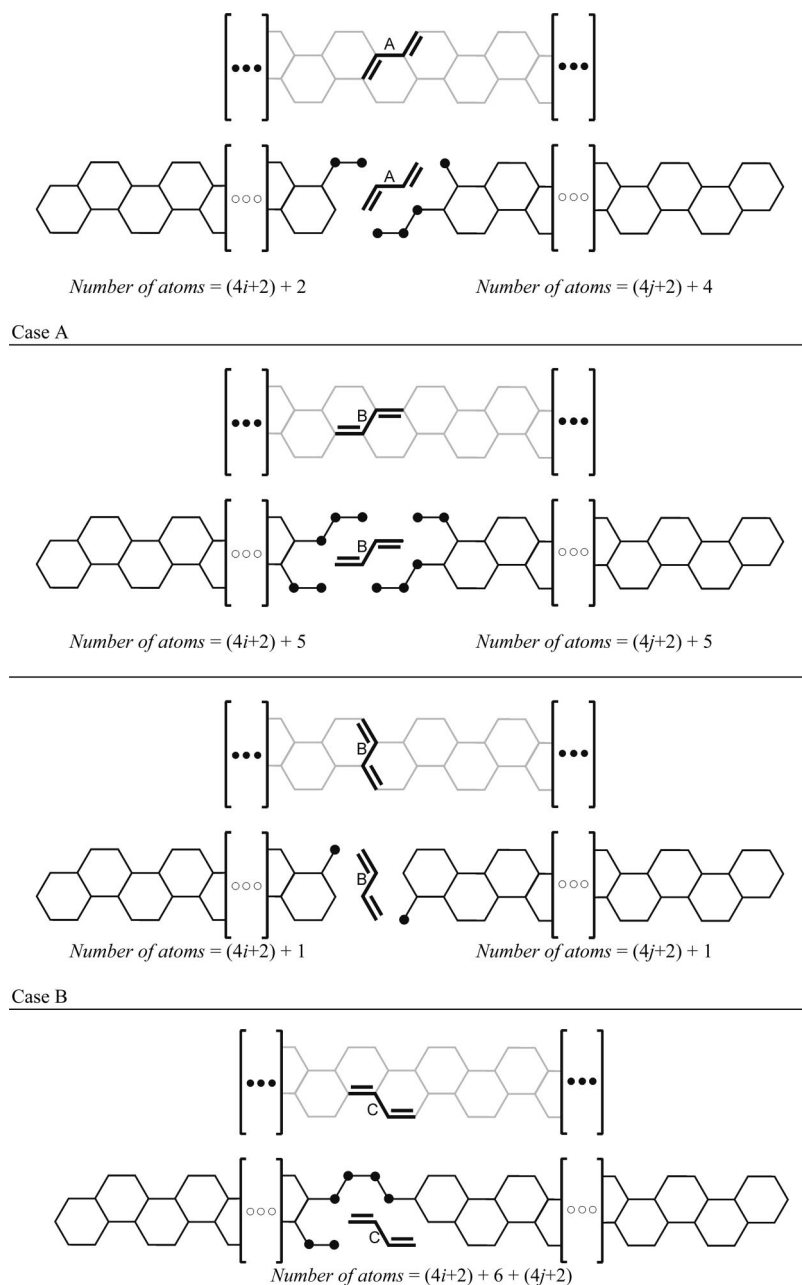
Chart 5



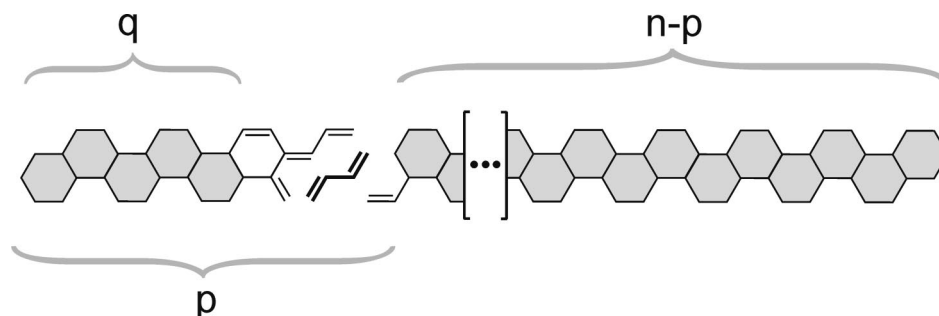
for their infinite chains. Figure 3 shows how the TMS values change for straight and kinked chains.

In both cases, the functions are monotonic and reach some limits: in the case of straight chains, the limit value of TMS is

Scheme 8



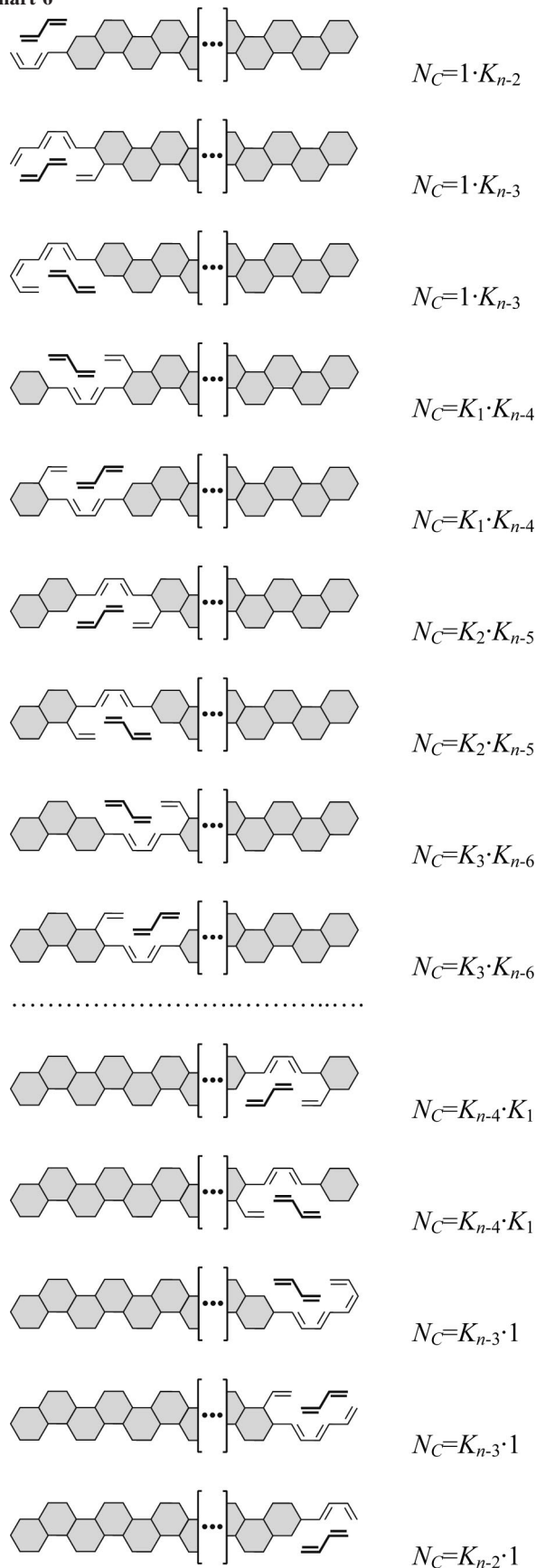
Scheme 9



equal to 0.333(3), whereas for kinked chains, the limit is 0.666(6). This means that the infinite chains of kinked benzenoid hydrocarbons should be thermodynamically significantly more stable than their straight isomers. For comparison, another infinite series of molecules known as zethrenes is added. Schemes in Table 1 present this kind of molecule.

This is a family which stems from perylene, and its first representative is named zethrene. If the chain linking two naphthalene molecules is elongated, then we find that there is a localization of single/double bonds along this chain. If we consider TMS for whole molecules plotted against the number of rings of the chain, we find out that TMS values

Chart 6



fall down and have to reach 0 in infinity. This is due to an obvious fact that, for two moieties of naphthalene at the beginning and the end of the infinite molecule, there is an infinite number of trans-type fragments, whereas the number

of cis ones is limited to those from naphthalenes, that is, $2 \times 14 = 28$, and the general formula for $TMS = 10/(3n - 1)$, where n is the number of rings. If $n \rightarrow \infty$, then TMS reaches zero. Figure 3 presents the plot of TMS versus the number of benzene rings.

It may be concluded that the topological approach based on a very simple counting of cis and trans fragments and then used in calculating TMS allows one not only to estimate the stability of a variety of benzenoid hydrocarbons but also, via mathematical procedures, to end up with statements about the stability of some infinite molecules. Moreover, it allows one to indicate that the stability of those infinite molecules may depend dramatically on the shape of the chains (kinked or straight) or the terminating fragments (naphthalene moieties in the last case).

In the Appendix is given the methodology of derivation of the formulas for TMS values for infinite chains.

Chart 7

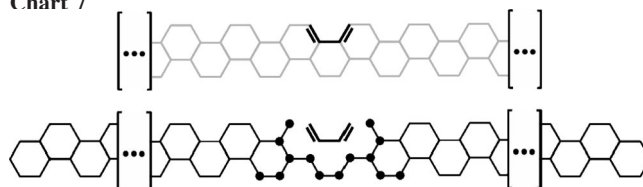
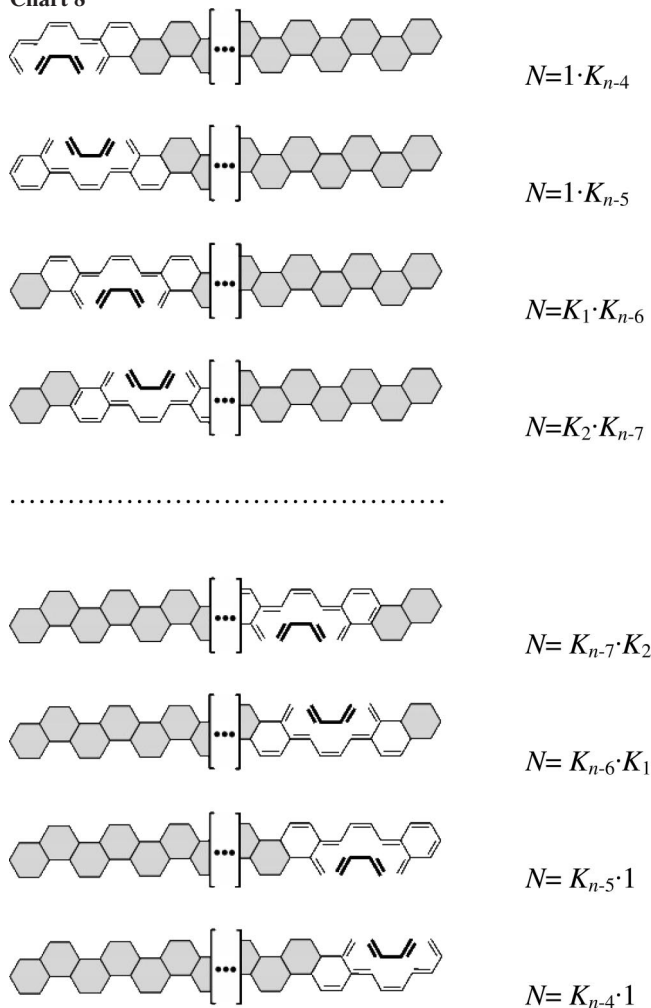


Chart 8



ACKNOWLEDGMENT

This work is dedicated to Professors Maria and Edward Dutkiewicz of the University of Adam Mickiewicz in Poznań, Poland.

APPENDIX

Consider first the case of infinite, **straight** benzenoid hydrocarbon with n delocalized rings (marked gray in Chart 1) and K_n canonical structures.

Note that the *trans* fragments may be oriented in relation to the molecule in two ways. The *trans* fragment consists of one single bond, which may be located either along the peripheral bonds (A) of the system or as a bridge between two peripheral chains of bonds (B). For the purpose of better illustration, let us look at the problem as shown in Chart 2.

The presented *trans* structures have equivalent symmetrical orientations. Localization of the fragment as in the A case leaves the system with an even number of π electrons $(4i + 2) + 6 + (4j + 2)$. Whereas in the B case, there is an odd number of π electrons in both substructures which are not connected with each other: $(4i + 2) + 1$ and $(4j + 2) + 1$. In the latter case, there is no possibility of drawing any canonical structure with the *trans* fragment. The important conclusion is that only A cases may be considered for further evaluation.

If we localize one *trans* fragment at one end of the chain, we obtain a system with $(n - 2)$ delocalized rings. The number of *trans* fragments, N_A , in a given position is equal to the number of canonical structures in the remaining delocalized fragment of the molecule, $N_A = K_{n-2}$ (see Chart 3). In a similar way we can find the number of *trans* fragments in any position in the chain (see Chart 4).

For a straight polyacene, the formula describing the number of canonical structures as a function of the number of rings reads

$$K_n = n + 1 \quad (2)$$

The number of single bonds in a particular canonical structure is

$$N_{\text{singlebonds}} = 3n \quad (3)$$

where n is the number of rings.

As already mentioned, the number of *cis* and *trans* fragments is related to the product of K_n and the number of single bonds; hence, the number of *cis* fragments is

$$N_{\text{cis}} = K_n N_{\text{singlebonds}} - N_{\text{trans}} \quad (4)$$

The number of *trans* fragments may be represented by a series which results from the schemes presented in Scheme 5. The total number of *trans* fragments for one orientation is given by a sum:

$$N_{\text{trans}} = 1 + K_1 + K_2 + K_3 + \dots + K_{n-4} + K_{n-3} + K_{n-1} = 1 + 2 + 3 + 4 + \dots + (n-3) + (n-2) + (n-1) \quad (5)$$

Taking into account four symmetrically equivalent orientations, we end up with the formula

$$N_{\text{trans}} = 4 \cdot \sum_{i=1}^{n-1} i = 2n(n-1) \quad (6)$$

When eq 6 is applied, the number of *cis* fragments is

$$N_{\text{cis}} = K_n 3n - 2n(n-1) = (n+1)3n - 2n(n-1) = n^2 + 5n \quad (7)$$

Thus, we can calculate TMS for an infinite chain of straight polyacenes:

$$\text{TMS} = \frac{N_{\text{cis}}}{N_{\text{cis}} + N_{\text{trans}}} = \frac{n^2 + 5n}{3n^2 + 3n} \quad (8)$$

and finally

$$\lim_{n \rightarrow \infty} \text{TMS} = \lim_{n \rightarrow \infty} \frac{N_{\text{cis}}}{N_{\text{cis}} + N_{\text{trans}}} = \lim_{n \rightarrow \infty} \frac{n^2 + 5n}{3n^2 + 3n} = \frac{1}{3} \quad (9)$$

Consider now the case of an infinite, **kinked** benzenoid hydrocarbon with n delocalized rings (marked gray in Scheme 6) and K_n canonical structures.

Note that the *trans* fragments may be oriented in relation to the molecule in three ways with bonds A, B, or C being the central bond of the *trans* fragment. The D bond may be involved only in the *cis* fragment. This is presented in Scheme 7.

Similarly to the previous case, it is sufficient to consider only the number of *trans* fragments. The *trans* fragment consists of one single bond (A, B, or C), which may be located along the peripheral bonds (A or C) of the system or as a bridge between two peripheral chains of bonds (B). For the purpose of better illustration, let us look at the problem as shown in Scheme 8.

The presented *trans* structures have equivalent symmetrical orientations. If the localization of the fragment is as in case A, the systems remain with even numbers of π electrons $(4i + 2) + 2$ and $(4j + 2) + 4$. A similar situation is in case C, where the localization of the *trans* fragment leaves the system with an even number of π electrons $(4i + 2) + 6 + (4j + 2)$. In the B case, however, two orientations of *trans* fragments are possible: a horizontal one and a vertical one. In both cases, localization of *trans* fragments leaves two systems with odd numbers of π electrons, that is, $(4i + 2) + 5$ and $(4j + 2) + 5$ for the horizontal orientation and $(4i + 2) + 1$ and $(4j + 2) + 1$ for the vertical orientation. It results from this consideration that neither of the B cases can be realized because the left and right fragments consist of an odd number of π electrons and no Kekule-type structure can be formed. The important conclusion is that only A and C cases may be considered for further evaluation. The localization of the *trans* fragment in an infinite kinked hydrocarbon with n rings and K_n canonical structures (as in the A and C cases) leads to the formation of two benzenoid subsystems with q and $n-p$ rings and K_q and K_{n-p} canonical structures (Scheme 9). Hence, the number of *trans* structures in such a position equals

$$N_{\text{trans}} = K_q K_{n-p} \quad (10)$$

Similarly to the case of straight polyacene, we construct a series of infinite molecules in which the *trans* fragment (case A) is localized, as in Chart 5. The total number of *trans* fragments in case A is equal to

$$N_{\text{trans}}^{\text{total}} = 2 \cdot 1 K_{n-3} + 2 \cdot 1 K_{n-4} + 2 \sum_{i=1}^{n-5} K_i K_{n-i-4} + 2 K_{n-4} \cdot 1 + 2 K_{n-3} \cdot 1 \quad (11)$$

The symmetry of two possible orientations results in a factor of 2 before the sign of the sum. It is known that the number of canonical structures K_n for kinked polyacenes (known also as fibonacenes¹⁹) with n rings is described by F_{n+2} ,²⁰ where F_i is Fibonacci number: $F_0 = 0$; $F_1 = 1$; $F_2 = 1$; $F_3 = 2$; $F_4 = 3$; $F_5 = 5$; $F_6 = 8$; [...] $F_n = F_{n-2} + F_{n-1}$. Hence,

$$\text{total} N_A = 2 \sum_{i=1}^{n-1} F_i F_{n-i} \quad (12)$$

Similarities to case C follow, see Chart 6. The total number of trans fragments for case C is equal to

$$\text{total} N_C = 1 \cdot K_{n-2} + 2 \cdot 1 \cdot K_{n-3} + 2 \sum_{i=1}^{n-4} K_i K_{n-i-3} + 2 \cdot K_{n-3} \cdot 1 + 1 \cdot K_{n-2} \quad (13)$$

Hence,

$$\text{total} N_C = 2 \sum_{i=2}^{n-1} F_i F_{n-i+1} + 2 \cdot F_1 F_n = 2 \sum_{i=1}^{n-1} F_i F_{n-i+1} \quad (14)$$

The overall summation leads to

$$\text{overall} N_{\text{trans}} = \text{total} N_A + \text{total} N_C \quad (15)$$

$$N_{\text{trans}} = 2 \sum_{i=1}^{n-1} F_i F_{n-i} + 2 \sum_{i=1}^{n-1} F_i F_{n-i+1} = 2 \sum_{i=1}^{n-1} F_i (F_{n-i} + F_{n-i+1}) \quad (16)$$

Applying the property of Fibonacci numbers,

$$F_n + F_{n+1} = F_{n+2} \quad (17)$$

we simplify eq 16

$$N_{\text{trans}} = 2 \sum_{i=1}^{n-1} F_i F_{n-i+2} \quad (18)$$

Applying another property of Fibonacci numbers,²¹

$$\sum_{K=0}^N F_K F_{N-K} = \frac{1}{5} (NL_N - F_N) \quad (19)$$

noting that

$$\sum_{K=1}^N F_K F_{N-K} = \frac{1}{5} (NL_N - F_N) \quad (20)$$

also, because $F_0 = 0$, where L_i is Lukas number, $L_1 = 1$; $L_2 = 3$; $L_3 = 4$; $L_4 = 7$; $L_5 = 11$; $L_6 = 18$; [...] $L_n = L_{n-2} + L_{n-1}$, and substituting into eq 18

$$n + 2 = m \quad (21)$$

we obtain

$$N_{\text{trans}} = 2 \sum_{i=1}^{m-3} F_i F_{m-i} \quad (22)$$

That is equal to

$$\begin{aligned} N_{\text{trans}} &= 2 \sum_{i=1}^{m-3} F_i F_{m-i} = 2 \sum_{i=1}^m F_i F_{m-i} - \\ &2 \left(\underset{\ddot{1}}{F_{m-2} F_2} + \underset{\ddot{1}}{F_{m-1} F_1} + \underset{\ddot{0}}{F_m F_0} \right) \\ &= 2 \left[\sum_{i=1}^m F_i F_{m-i} - (F_{m-1} + F_{m-2}) \cdot 1 \right] \\ &= 2 \left(\sum_{i=1}^m F_i F_{m-i} - F_m \right) = 2 \left[\frac{1}{5} (mL_m - F_m) - F_m \right] \end{aligned} \quad (23)$$

And finally,

$$N_{\text{trans}} = 2 \left\{ \frac{1}{5} [(n+2)L_{n+2} - F_{n+2}] - F_{n+2} \right\} \quad (24)$$

$$N_{\text{cis}} = 3nK_n - N_{\text{trans}} = 3nF_{n+2} - N_{\text{trans}} = 3nF_{n+2} - 2 \left\{ \frac{1}{5} [(n+2)L_{n+2} - F_{n+2}] - F_{n+2} \right\} \quad (25)$$

Now, we have a formula which presents the number of all cis fragments. However, in order to apply the formula for TMS (eq 1), we have to determine the number of *cis*(bay). To do so, we have to consider the following situation (see Chart 7).

Localization of the cis fragment in the so-called “bay region” leaves the system that consists of $(4i+2) + 14 + (4j+2)$ atoms, where black circles indicate the atoms not involved in π -electron delocalization. In this way, we obtain a molecule with two delocalized subsystems with $4i+2$ and $4j+2$ π electrons.

As a result of localization of the *cis*(bay) fragment from the beginning of the chain up to the end on another end of it, we obtain a series of structures for which the number of *cis*(bay) ($N_{\text{cis}}^{\text{bay}}$) is equal to the product of the Kekule structure numbers $K_i K_j$ of the delocalized subsystems (marked in gray, Chart 8). The number of bay-regions is less by two than the number of rings n . Therefore, the total number of *cis*(bay) equals

$$N_{\text{cis}}^{\text{bay}} = \sum_{i=1}^{n-2} F_i F_{n-1-i} = \frac{1}{5} [(n-1)L_{n-1} - F_{n-1}] = \frac{1}{5} [(5n-3)F_{n+2} - (2n-1)L_{n+2}] \quad (26)$$

The overall measure of stability for kinked polyacene with n rings is

$$\text{TMS} = \frac{N_{\text{cis}} - N_{\text{cis}}^{\text{bay}}}{N_{\text{cis}} + N_{\text{trans}}} = \frac{2nF_{n+2} - L_{n+2} + 3F_{n+2}}{3nF_{n+2}} = \frac{2}{3} - \frac{L_{n+2}}{3nF_{n+2}} + \frac{1}{n} \quad (27)$$

For infinite kinked polyacene, we obtain

$$\lim_{n \rightarrow \infty} \text{TMS} = \lim_{n \rightarrow \infty} \frac{N_{\text{cis}} - N_{\text{cis}}^{\text{bay}}}{N_{\text{cis}} + N_{\text{trans}}} = \lim_{n \rightarrow \infty} \left(\frac{2}{3} - \frac{L_{n+2}}{3nF_{n+2}} + \frac{1}{n} \right) = \frac{2}{3} \quad (28)$$

REFERENCES AND NOTES

- (1) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vol. 1-2.
- (2) Pauling, L. *The Nature of Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 195.
- (3) Dewar, M. J. S.; de Llano, C. Ground States of Conjugated Molecules. XI Improved Treatment of Hydrocarbons. *J. Am. Chem. Soc.* **1969**, *91*, 789–795.
- (4) Hess, B. A.; Schaad, L. J. Huckel Molecular Orbital π -Resonance Energies. The Benzenoid Hydrocarbons. *J. Am. Chem. Soc.* **1971**, *93*, 2413–2416.
- (5) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; J. Wiley: New York, 1961; p 240.
- (6) Cyranski, M. K. Energetic Aspects of Cyclic π -Electron Delocalization. *Chem. Rev.* **2005**, *105*, 3773–3811.
- (7) Randić, M. Aromaticity of Polycyclic Conjugated Hydrocarbons. *Chem. Rev.* **2003**, *103*, 3449–3505.
- (8) Clar, E. *The aromatic Sextet*; Wiley: New York, 1972.
- (9) Khadikar, P. V.; Singh, J.; Ingle, M. Topological Estimation of Aromatic Stabilities of Polyacenes and Helicenes: Modeling of Resonance Energy and Benzene Character. *J. Math. Chem.* **2007**, *42*, 443–446.

- (10) Wiener, H. Structural Determination of Paraffin Boiling Points. *J. Am. Chem. Soc.* **1947**, 69, 17–20.
- (11) Khadikar, P. V.; Deshpande, N. V.; Kale, P. P.; Dabrynin, A.; Gutman, I.; Domotor, G. The Szeged Index and an Analogy with the Wiener Index. *J. Chem. Inf. Comput. Sci.* **1995**, 35, 547–550.
- (12) Khadikar, P. V.; Karmarkar, S.; Agrawal, V. K.; Singh, J.; Shrivastava, A.; Lukovits, I.; Diudea, M. V. Szeged Index - Applications for Drug Modeling. *Lett. Drug Des. Discovery* **2005**, 2, 606–624.
- (13) Khadikar, P. V.; Singh, S.; Jaiswal, M.; Mandloi, D. Topological Estimation of Electronic Absorption Bands of Arene Absorption Spectra as a Tool for Modeling Their Toxicity Environmental Pollution. *Bioorg. Med. Chem. Lett.* **2004**, 14, 4795–4801.
- (14) Matta, C. F.; Hernandez, Trujillo, J.; Tang, T.-H.; Bader, R. F. W. Hydrogen-Hydrogen Bonding: A Stabilizing Interaction in Molecules and Crystals. *Chem.—Eur. J.* **2003**, 9, 1940–1951.
- (15) Bader, R. F. W. *Atoms in Molecules: A quantum theory*; Clarendon: Oxford, U. K., 1990.
- (16) Poater, J.; Visser, R.; Sola, M.; Bickelhaupt, M. Why Kinked is More Stable than Straight. *J. Org. Chem.* **2007**, 72, 1134–1142.
- (17) Randić, M. Conjugated Circuits and Resonance Energies of Benzenoid Hydrocarbons. *Chem. Phys. Lett.* **1976**, 38, 68–70.
- (18) Cyrański, M. K.; Stępień, B. T.; Krygowski, T. M. Global and Local Aromaticity of linear and Angular Polyacenes. *Tetrahedron* **2000**, 56, 9663–9667.
- (19) Balaban, T. A. Chemical Graphs. L. Symmetry and Enumeration of Fibonacenes (Unbranched Catacondensed Benzenoids Isoarithmic with Helicenes and Zigzag Catafusenes). *MATCH* **1989**, 24, 29–38.
- (20) Gutman, I.; Kavzar, S. Chemical Graph Theory of Fibonacenes. *MATCH* **2006**, 56, 637–648.
- (21) Weisstein, E. W. *CRC Concise Encyclopedia of Mathematics*; Chapman & Hall: Boca Raton, FL, 2003; p 1043.

CI800061Q