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On the Aromatic Stabilities of Polyacenes and Helicenes*

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The conjugated circuits model is used to predict the aromatic stabilities of polyacenes and helicenes. Helicenes are predicted to be always more stable than the corresponding polyacenes. This is supported by the available experimental findings.

INTRODUCTION

Polyacenes and helicenes represent two distinct classes of isomeric benzenoid hydrocarbons with a common molecular formula $C_NH_{(N+6)/2}$. Structurally they differ in the mode of annelation: polyacenes are linearly (para) annelated benzenoids which possess translational symmetry, whilst helicenes are angularly (ortho) annelated benzenoids which possess helical symmetry. Consequently, they differ considerably in their physical, chemical, and biological properties.[1,2] Chemistry of polyacenes and helicenes is still very much of interest to synthetic chemists, environmental chemists, cancer research chemists, theoretical chemists, analytical chemists, structural chemists, *etc.*[3–22]

We wish to report the application of the conjugated circuits model[23,24] to polyacenes and helicenes, and to predict their aromatic stabilities. The conjugated circuits model has been rather successfully applied to a variety of conjugated hydrocarbons,[23,25–28] their ions,[29–31] and even to heterocyclic systems.[32,33] This model has already been applied to the first four polyacenes.[23] Here we will report results for the higher polyacenes. In addition, the polyacenes will be used in this work for the comparison with helicenes. Besides we will produce some general results valid for both classes, and some of these results will also be novel for polyacenes.

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THE CONJUGATED CIRCUITS MODEL

The conjugated circuits model has been introduced for studying conjugation and aromaticity in polycyclic conjugated molecules. Graph theoretical analysis of Kekulé valence structures revealed that each Kekulé structure can be partitioned into several conjugated circuits.[23] Conjugated circuits have been defined as those circuits within individual Kekulé valence structure in which there is a regular alternation of a formal carbon-carbon single and double bonds. Thus, conjugated circuits are necessarily of even length.

The circuit decomposition of individual Kekulé structures of polyacenes and helicenes leads to (4n + 2) (n = integer) linearly independent, linearly dependent, and disconnected conjugated circuits. Linearly independent circuits are those that cannot be represented by a superposition of conjugated circuits of smaller size. As has been discussed elsewhere[34] the total number of all conjugated circuits within a single Kekulé valence structure is exactly K-1, where K is the number of Kekulé valence structures. Therefore, the total count of all conjugated circuits belonging to a given benzenoid hydrocarbon is given by $K \cdot (K - 1)$. The symbols R_n $(n = 1, 2, \ldots)$ are used for conjugated circuits (rings) of size $4n + 2$.

We will illustrate the above by an example. In Figure 1 we present the Kekulé structures of 3,4-benzophenanthrene.

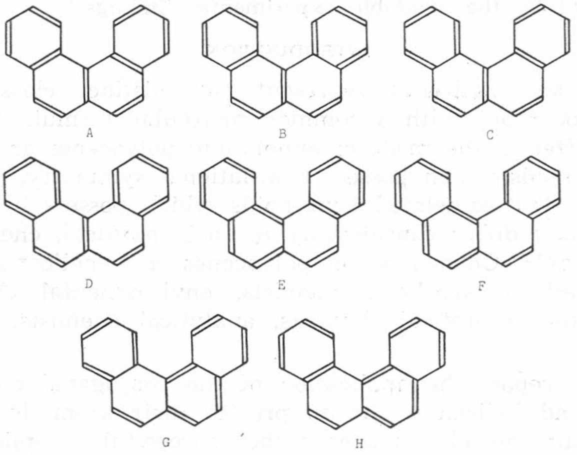


Figure 1. Kekulé valence structures of 3,4-benzophenanthrene.

In Table I we give the count of all conjugated circuits for the corresponding Kekulé structures of 3,4-benzophenanthrene.

In Figure 2 are depicted all conjugated circuits belonging to the Kekulé structure F of 3,4-benzophenanthrene (see Figure 1).

For calculating the resonance energies, RE, of polyacenes and helicenes we will use linearly independent and linearly dependent conjugated circuits.

TABLE I

The Conjugated Circuits Count for 3,4-Benzophenanthrene. The Corresponding Kekulé Structures are Given in Figure 1.

Kekulé structures	Conjugated circuits count
A	$4R_1 + 3\,(R_1 \cdot R_1)$
B	$3R_1 + R_2 + 2\,(R_1R_1) + (R_1R_2)$
C	$3R_1 + R_2 + 2\,(R_1R_1) + (R_1R_2)$
D	$2R_1 + 2R_2 + (R_1R_1) + 2(R_1R_2)$
E	$2R_1 + 2R_2 + R_3 + (R_1R_1) + (R_1R_2)$
F	$2R_1 + R_2 + R_3 + R_4 + (R_1R_1) + (R_1R_2)$
G	$2R_1 + R_2 + R_3 + R_4 + (R_1R_1) + (R_1R_2)$
H	$2R_1 + 2R_2 + R_3 + (R_1R_1) + (R_1R_2)$
Total count:	$20R_1 + 10R_2 + 4R_3 + 2R_4 + 12\,(R_1R_1) + 8\,(R_1R_2)$

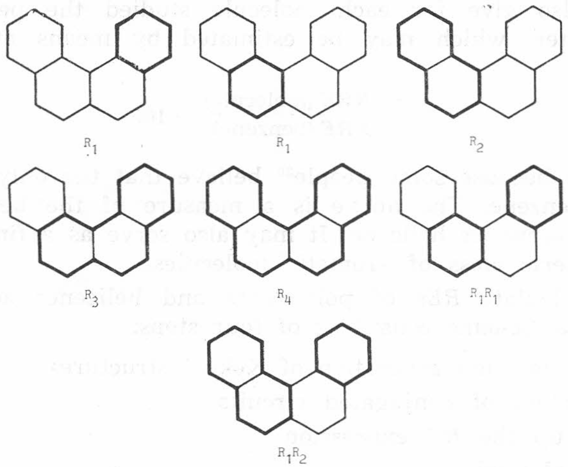


Figure 2. Conjugated circuits of the Kekulé structure F of 3,4-benzophenanthrene (see Figure 1.).

The expression for the molecular resonance energy may be obtained by adding the results for individual Kekulé valence structures and dividing the total by K,

$$RE = \frac{1}{K} \sum_{n} |R_n|\, R_n \tag{1}$$

where $|R_n|$ represents the number of R_n circuits for a given value of n. Only the first four members of the R_n series were previously considered.[23] The following values (based on the work by Dewar and de Llano[35] who carried out SCF π-MO RE calculations for a number of polycyclic conjugated hydrocarbons making thus possible to determine the values of R_n)[23] are adopted for the parameters R_n:

$$R_1 = 0.869 \text{ eV}$$

$$R_2 = 0.246 \text{ eV}$$

$$R_3 = 0.100 \text{ eV}$$

$$R_4 = 0.041 \text{ eV}$$

With these values *RE* of 3,4-benzophenanthrene is given by,

$$RE(\text{3,4-benzophenanthrene}) = \frac{1}{8}(20R_1 + 10R_2 + 4R_3 + 2R_4) = 2.09 \text{ eV} \qquad (2)$$

In the order to avoid the size effect, the *RE* is normalized,

$$NRE = \frac{RE}{N} \qquad (3)$$

where *NRE* stands for *RE* per π electron, whilst *N* is the number of π electrons in the conjugated molecule.

We will also give for each molecule studied the percentage of its benzene character, which may be estimated by means of the following formula,

$$\% = \frac{NRE\,(\text{molecule})}{NRE\,(\text{benzene})} \cdot 100 \qquad (4)$$

This is done so because some people[36] believe that the only truly aromatic compound is benzene. The above is a measure of the benzene character of a given polyacene or helicene. It may also serve as a finer classification within an isomeric class of aromatic molecules.

We will calculate *RE*s of polyacenes and helicenes according to the following general scheme consisting of four steps:

(1) Enumeration and generation of Kekulé structures
(2) Enumeration of conjugated circuits
(3) Setting up the *RE* expression
(4) Numerical work.

ENUMERATION OF KEKULÉ STRUCTURES FOR POLYACENES AND HELICENES

Since both polyacenes and helicenes possess regular structures with the same repeating unit, explicit formulae for the *enumeration* of their Kekulé structures may be given.

(a) Polyacenes

$$\mathrm{K} = \mathrm{H} + 1 \qquad (5)$$

where K and H are, respectively, the number of Kekulé structures and the number of rings of a given polyacene. Therefore, the Kekulé numbers for polyacenes represent a set of natural numbers starting with K = 1 for a hypothetical benzenoid hydrocarbon with H = 0. The above formula was first obtained by Gordon and Davison.[37]

(b) Helicenes

$$K_H = K_{H-1} + K_{H-2}; \quad H = 2, 3, 4, \ldots \tag{6}$$

$$K_0 = 1 \text{ (by definition)} \tag{7}$$

$$K_1 = K \text{ (benzene)} = 2 \tag{8}$$

where K and H are, respectively, the number of Kekulé structures and the number of rings of a given helicene.

The inspection of Kekulé numbers for helicenes (2, 3, 5, 8, 13, 21, 34, 55, ...) reveals that these numbers belong to the Fibonacci series (1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, ...).[38] The Fibonacci numbers F_j can be generated by the formula $F_j = F_{j-1} + F_{j-2}$. Thus, formula (6) may serve formally as a generator for the Fibonacci numbers assuming (7) and $K_{-1} = 1$. Similar observations for phenanthrene series have been made by Randić[27] and Cyvin[39], and by Balaban and Tomescu[17] for any isoarithmic catafusene system.

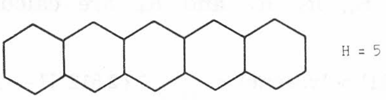
Generation of individual Kekulé structures may be carried out by several procedures.[40,41] In the present work we generated the Kekulé structures of polyacenes and helicenes by hand starting from the simplest molecule in the set and gradually deriving Kekulé structures of more complex molecules from the known set of Kekulé structures of simpler molecules. However, we needed Kekulé structures explicitly only for the first few molecules in the series in order to check the regularity of the pattern which also emerges in the conjugated circuits count.

THE CONJUGATED CIRCUITS COUNT FOR POLYACENES AND HELICENES

The conjugated circuits for polyacenes may be enumerated by means of the following counting formula,[42]

$$|R_n| = 2\,[H - (n - 1)]; \quad n = 1, 2, 3, 4 \tag{7}$$

where the symbols have their previous meaning. The above formula reveals that the number of conjugated circuits in the linear polyacenes is dependent only on the number of the rings in the molecule. As an example we will apply the above formula to pentacene (see Figure 3).



pentacene

$$|R_1| = 2\,5 = 10, \quad |R_2| = 2\,(5 - 1) = 8, \quad |R_3| = 2\,(5 - 2) = 9, \quad |R_4| = 2\,(5 - 3) = 4$$

Total count: $10\,R_1 + 8\,R_2 + 6\,R_3 + 4\,R_4$

$$RE = (1/8)\,(10\,R_1 + 8\,R_2 + 6\,R_3 + 4\,R_4) = 1.43 \text{ eV}$$

Figure 3. Application of the polyacene circuits counting formula to pentacene.

In the case of the circuits count for helicenes we found that it is enough to know the number of R_1-circuits, the others (R_2, R_3, R_4) are related to them according to the following set of rules,

$$|R_2\,(H)| = |R_1\,(H - 1)| \tag{9}$$

$$|R_3\,(H)| = |R_2\,(H - 1)| = |R_1\,(H - 2)| \tag{10}$$

$$|R_4\,(H)| = |R_3\,(H - 1)| = |R_2\,(H - 2)| = |R_1\,(H - 3)| \tag{11}$$

where H is the number of hexagons in the [H]-helicene. The R_1-circuits may be enumerated according the following recursive formulae,

$$|R_1(\mathrm{H})| = |R_1(\mathrm{H}-1)| + |R_1(\mathrm{H}-2)| + 2\mathrm{K}(\mathrm{H}-2); \quad \mathrm{H} = 2, 3, \ldots \tag{12}$$

where $|R_1(\mathrm{H}-1)|$ and $|R_1(\mathrm{H}-2)|$ are, respectively, the R_1-circuits counts for [H — 1] helicene and [H — 2] helicene, whilst K (H — 2) is the Kekulé structure count for the [H — 2] helicene. Formally the R_1 for the [0]helicene is 1 by definition and for [1]helicene (benzene) is 2. R_2, R_3 and R_4 for [0]helicene and [1]helicene are all zero, R_3 and R_4 are zero for [2]helicene, whilst R_4 is zero for [3]helicene, respectively. Similar formulae for the circuits count in helicenes have also been derived by Balaban and Tomescu.[42a]

In Table II we give the circuits counts for [N]helicenes up to N = 8.

TABLE II

The Conjugated Circuits Count for Helicenes

[H]-helicene	K	$\vert R_1\vert$	$\vert R_2\vert$	$\vert R_3\vert$	$\vert R_4\vert$
1	2	2			
2	3	4	2		
3	5	10	4	2	
4	8	20	10	4	2
5	13	40	20	10	4
6	21	76	40	20	10
7	34	142	76	40	20
8	55	260	142	76	40

RESULTS AND DISCUSSION

Diagrams of studied polyacenes and helicenes are given in Figure 4. *RE*, of polyacenes, except for the first four which were used to obtain the parametric values for R_1, R_2, R_3, and R_4, are calculated by means of the simple formula,

$$RE\,([\mathrm{H}]\ \text{polyacene}) = \frac{1}{\mathrm{H}+1}\{2.512\ \mathrm{H} - 1.138\} \tag{13}$$

where H is the number of hexagons in the polyacene.

The *RE*s of helicenes have been calculated using the following formula:

$$RE\,([\mathrm{H}]\ \text{helicene}) = \frac{1}{\mathrm{K}(\mathrm{H}-1) + \mathrm{K}(\mathrm{H}-2)}\{1.115\ R_1(\mathrm{H}-1) +$$

$$+ 0.969\,|R_1(\mathrm{H}-2)| + 0.041\,|R_1(\mathrm{H}-3)| + 1.738\mathrm{K}(\mathrm{H}-2)\} \tag{14}$$

where the symbols have their previous meaning. Both expressions (13) and (14) have been derived from (1) by introducing the appropriate terms for K (H), $|R_n(\mathrm{H})|$, and R_n(H).

Calculated resonance energies of polyacenes and helicenes are given in Table III.

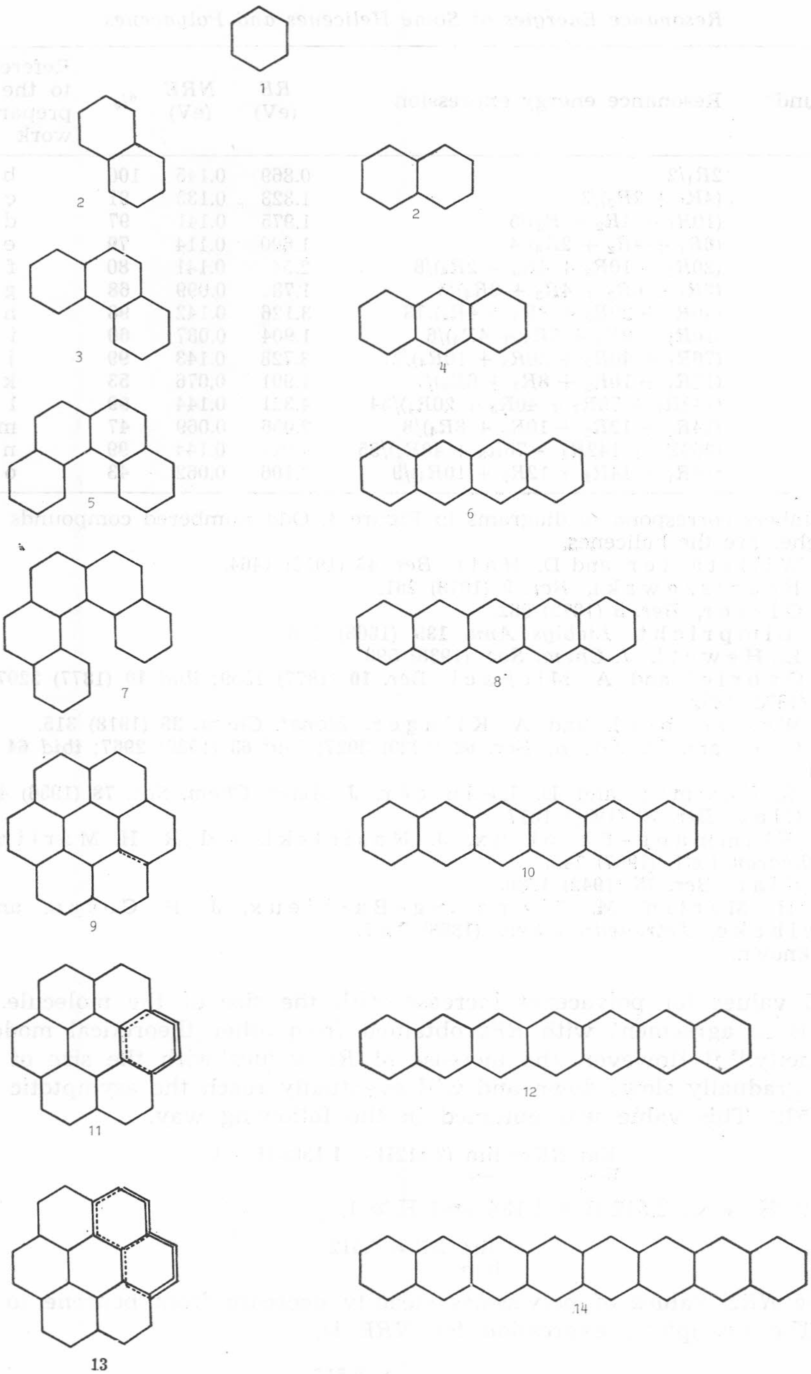


Figure 4. Diagrams of considered helicenes and polyacenes.

TABLE III

Resonance Energies of Some Helicenes and Polyacenes

Compound[a]	Resonance energy expression	*RE* (eV)	*NRE* (eV)	%	Reference to the preparative work
1	$2R_1/2$	0.869	0.145	100	b
2	$(4R_1 + 2R_2)/3$	1.323	0.133	91	c
3	$(10R_1 + 4R_2 + R_3)/5$	1.975	0.141	97	d
4	$(6R_1 + 4R_2 + 2R_3)/4$	1.600	0.114	79	e
5	$(20R_1 + 10R_2 + 4R_3 + 2R_4)/8$	2.54	0.141	80	f
6	$(8R_1 + 6R_2 + 4R_3 + 2R_4)/5$	1.78	0.099	68	g
7	$(40R_1 + 20R_2 + 8R_3 + 4R_4)/13$	3.126	0.142	98	h
8	$(10R_1 + 8R_2 + 6R_3 + 4R_4)/6$	1.904	0.087	60	i
9	$(76R_1 + 40R_2 + 20R_3 + 10R_4)/21$	3.728	0.143	99	j
10	$(12R_1 + 10R_2 + 8R_3 + 6R_4)/7$	1.991	0.076	53	k
11	$(142R_1 + 76R_2 + 40R_3 + 20R_4)/34$	4.321	0.144	99	l
12	$(14R_1 + 12R_2 + 10R_3 + 8R_4)/8$	2.056	0.069	47	m
13	$(260R_1 + 142R_2 + 76R_3 + 40R_4)/55$	4.911	0.144	99	n
14	$(16R_1 + 14R_2 + 12R_3 + 10R_4)/9$	2.106	0.062	43	o

a. Numbers correspond to diagrams in Figure 4. Odd numbered compounds 3 and higher are the helicenes.
b. R. Willstätter and D. Hatt, *Ber.* **45** (1912) 1464.
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m. E. Clar, *Ber.* **75** (1942) 1330.
n. R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *Tetrahedron Lett.* (1968) 3507.
o. unknown.

RE values for polyacenes increase with the size of the molecule. This result is in agreement with *RE*s obtained from other theoretical models of aromaticity.[46-49] However, the increase of *RE* values with the size of polyacenes gradually slows down and will eventually reach the asymptotic value of ≈2.512. This value was obtained in the following way,

$$\lim_{H \to \infty} RE = \lim_{\to \infty} (2.512H - 1.138)/H + 1 \tag{15}$$

Since at $H \to \infty$, $2.512\,H \gg 1.138$ and $H \gg 1$,

$$\lim_{H \to \infty} RE = 2.512 \tag{16}$$

The *NRE* values of polyacenes steadily decrease from benzene to octacene. The asymptotic expression for *NRE* is,

$$\lim_{N \to \infty} NRE = \frac{2.512}{N}\,. \tag{17}$$

It is obtained by considering the *RE* expression (13) and the relationship between N and H,

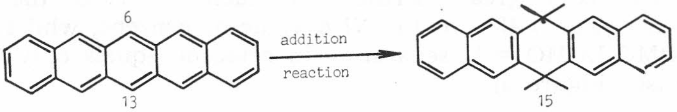
$$H = \frac{1}{4}(N - 2) \tag{18}$$

The *RE* of (13) expressed in terms of number of atoms N instead of the number of rings H in a polyacene is given by,

$$RE = \frac{1}{N + 2}\{2.512\,N - 9.576\}. \tag{19}$$

The percentage of the benzene character rapidly decreases and thus follows the decrease in the stability of polyacenes with the increase in the size.[1]

Higher polyacenes easily undergo addition reactions for example with maleic anhydride.[1,50] Thus, pentacene undergoes addition reactions at the 6 and 13 positions to yield 6,13-dihydropentacene derivatives which now contain two naphthalene subunits:



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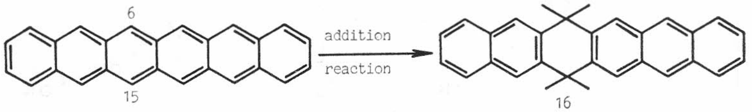
It appears that the formation of two new σ bonds in addition to the increased *NRE* (from 0.087 in pentacene to 0.266 in 6,13-dihydropentacene) of the remaining π electrons is more than enough to offset the loss of two π bonds

In diagrams 15—18 we give single Kekulé structures for the subunits but the calculations are based on all Kekulé valence structures of the corresponding polyacenes.

Hexacene is the most reactive benzenoid which can be obtained in a pure state.[1] It must be kept in vacuum. Hexacene easily undergoes additional reactions producing 6,15-dihydrohexacene derivatives which contain as subunits naphthalene (*NRE* = 0.133) and anthracene (*NRE* = 0.114):



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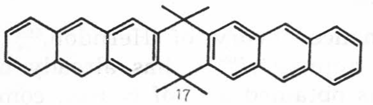
6,15-dihydrohexacene derivative should be considerably more stable than the parent structure judging from the comparison of their *NRE* values: 0.076 (*10*) *vs.* 0.133 + 0.114 (*16*).

The next member of the polyacene family heptacene is so reactive that is not possible to obtain it in a pure state.[1] The 7,16-dihydroheptacene derivative is much more stable structure than the parent compound.



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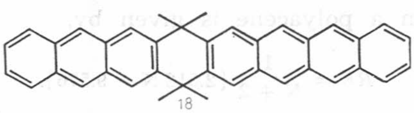
Comparison of *NRE* values (0.069 (*12*) *vs.* 0.114 + 0.114 (*17*)) again favours the 7,16-dihydroheptacene derivative.

The last polyacene considered here is octacene. This benzenoid hydrocarbon is unknown. All synthetic efforts to make it have failed, presumably because of its extreme reactivity. In this case again *NRE* values favour the 8,17-dihydrooctacene derivative over the parent hydrocarbon: (0.062 (*9*) *vs.* 0.114 + 0.099 (*18*))



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The higher members of the polyacene series: nonacene, decacene, undecacene *etc.* would have the corresponding dihydro-derivatives so reactive that even these structures could not be obtained. From all the evidence that exists in the literature it follows that the polyacenes represent a class of aromatic molecules for which the thermodynamic stability gradually diminishes with increasing size while reactivity (*e. g.*, addition reactions) increases dramatically. This is so because the aromaticity does not necessarily also enforce a great inertness to reactivity. Thus, the *NRE* value of octacene is equal to 43% of the *NRE* value of benzene, whilst the frontier orbitals (HOMO-LUMO = Δ) separation in octacene equals only 11% of that in benzene (see Figure 5).

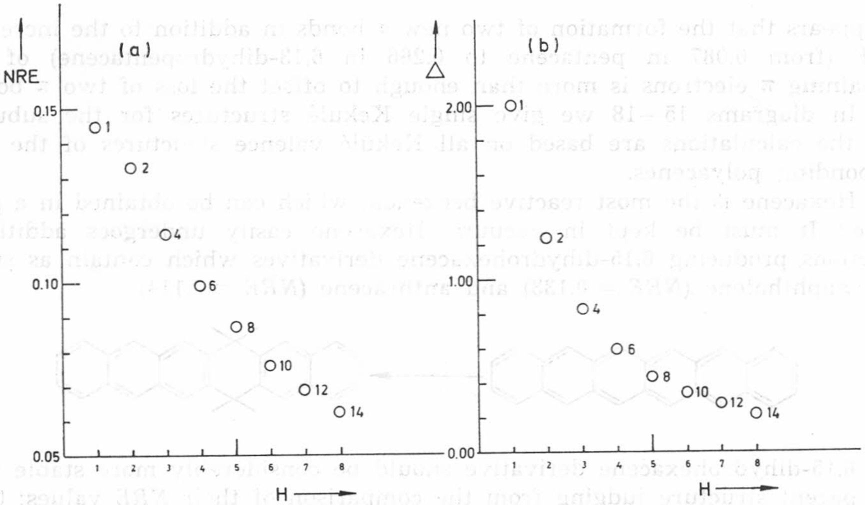


Figure 5. (a) *NRE vs.* H and (b) Δ = HOMO — LUMO *vs.* H for polyacenes. Numbers correspond to diagrams in Figure 4.

The preparative problems with polyacenes are evidently due to high reactivity of these compounds.

The structure-resonance theory of Herndon,[50a] which is equivalent to the conjugated circuits approach,[50b,50c] has already been carried out for the polyacenes,[50d] the results obtained are, of course, comparable to ours.

The situation is quite different with helicenes. Helicenes are predicted to be of high aromatic stability. The aromatic stability is so high in helicenes (almost, according to the *NRE* criterion, equal to that of benzene) that the considerable steric interactions pushing the overlapping terminal rings apart[2] cannot harm the molecule (although in the higher systems this may become an important destabilizing contribution to the energetics of the helicene system). A given helicene in comparison with the corresponding isomeric polyacene is always a more stable system (see Table IV).

TABLE IV

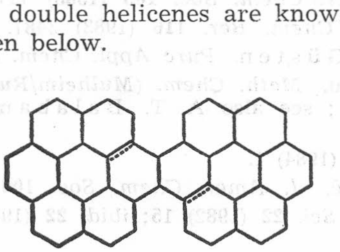
Difference in RE and NRE Values Between Isomeric Polyacenes and Helicenes

Helicene — polyacene	ΔRE	ΔNRE
3—4	0.375	0.027
5—6	0.76	0.042
7—8	1.222	0.055
9—10	1.737	0.067
11—12	2.265	0.075
13—14	2.805	0.082

More generally, the benzenoid systems with *ortho*-annelated rings are always more stable than the corresponding systems with *para*-annelated rings. Thus, it is experimentally established[1] that phenanthrene is more stable than anthracene, 3.4-benzophenanthrene than tetracene, and 3.4,5.6-dibenzophenanthrene than pentacene, respectively. The conjugated circuits model is fully in accordance with this observation.

NRE values (and the percentage of the benzene character) indicate that the helicenes remain rather highly aromatic with the increase in the size. Since the polyacenes become less and less aromatic with the increase in the size, the difference in *RE* (and *NRE*) between helicenes and polyacenes becomes larger and larger (see Table IV). The complete series of helicenes through [14]helicene has been synthesized. Further progress appears to be limited by the patience of the investigators rather than the stability of the product.

Several double helicenes are known.[51,52] Two examples of double helicenes are given below.



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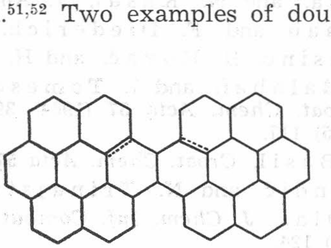

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We can immediately assign to both of them their Kekulé number, which is 377. The total count of conjugated circuits for them is enormous, *i. e.* 141,752. This count includes R_n circuits with $n > 4$ and all other possibilities. However, we calculated their *RE*s by expression (14). Since both structures have the same circuits count and they have the same (and very high) value of *RE* (7.27) and *NRE* (0.145), respectively.

Finally we point out that there is some similarity between this study and the work by Seitz *et al.*[53] where there is included a comparison of polyacenes and »polyphenanthrenes«. (This later family is that of the single-chain catafusenes with phenanthrene twists in alternating directions, rather than in the same directions as for helicenes.) Within the approximations used the helicenes and polyphenanthrenes have the same *RE*'s. The qualitative conclusions concerning the *RE*'s per electron are much the same, though in place of the conjugated circuits approach the related Pauling-Wheland resonance theory is used.[54,55]

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SAŽETAK

O aromatičkoj stabilnosti poliacena i helicena

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Model konjugiranih krugova upotrijebljen je za predviđanje aromatičke stabilnosti poliacena i helicena. Predviđeno je da su heliceni uvijek stabilniji od odgovarajućih policena. To je predviđanje poduprto postojećim eksperimentalnim rezultatima.