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Aromatic Stabilities of Bridged Polyenes*

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The aromatic stabilities of bridged polyenes have been studied by means of the topological (graph-theoretical) resonance energy (TRE) model developed by the Zagreb Group a decade ago. The aromatic stabilities of bridged polyenes are compared with those predicted earlier for polyenes, annulenes, bridged annulenes, and polyacenes. This comparison has produced the following aromatic stability order:

polyenes $<$ annulenes $<$ bridged polyenes
$<$ bridged annulenes $<$ polyacenes.

The available experimental findings support this prediction.

INTRODUCTION

In the present work we wish to report some studies on the aromatic stability of bridged polyenes, for which the descriptive name, "hairpin" polyenes[1] has been suggested. We will use both of the terms bridged polyenes and "hairpin" polyenes indiscriminately in this work. The synthesis, UV-visible absorption, polarized fluorescence, and MCD spectra of six "hairpin" polyenes have recently been reported.[2]

The bridged polyenes may be formally constructed from linear polyenes by forcing them to adopt a U-shape (all-trans conformation) by suitable bridging. Theoretically it appears possible to construct bridged polyenes from a closely related class of bridged annulenes by removing one of the perimeter bonds and thus interrupting the cyclic conjugation. The open end may be left as it is or a convenient group may be used to bridge it. In this way two classes of "hairpin" polyenes may be generated: One class (Class a) of bridged

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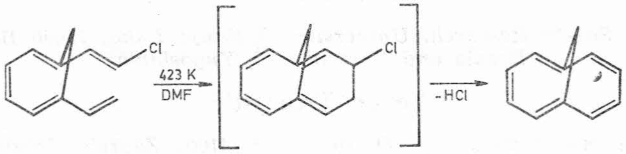
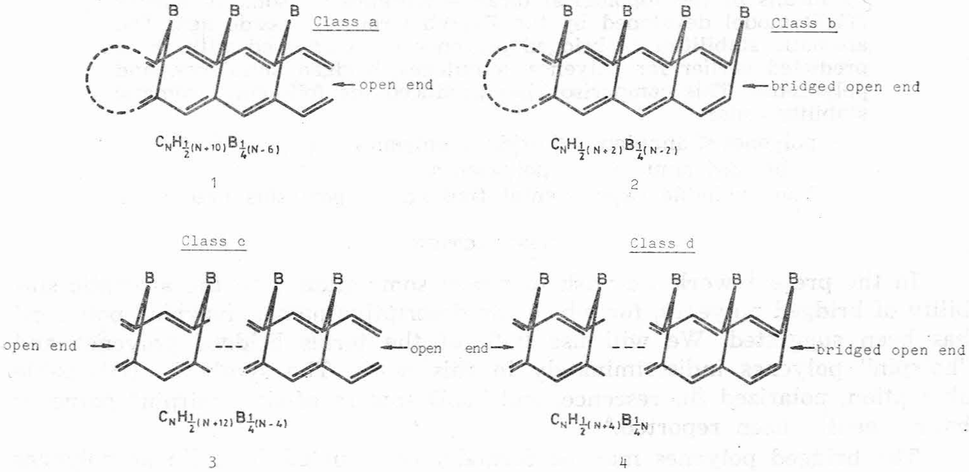
polyenes has an open end (structure *1* in Figure 1) and this open end is also bridged in the other class (Class b) (structure *2* in Figure 1).

The reverse process, i. e. producing bridged annulenes from the related bridged polyenes by an electrocyclic annelation is experimentally known.[3] Thus, the lower members of Class a may be used to produce the bridged annulenes. An example of such a process is the preparation of bridged[10]-annulene from the corresponding bridged polyene: heating the chloro-derivative of bridged[10]polyene in dimethylformamide yields bridged[10]annulene by a 10 π-electrocyclic process combined with elimination of hydrogen chloride from the labile 3,4-dihydro-1,6-methano[10]annulene intermediate:[4]



Bridged[14]annulene, bridged[18]annulene, and even bridged[22]annulene are also prepared by this strategy.

Two more classes of bridged polyenes can likewise be imagined: One such class (Class c) will have both ends open (structure *3* in Figure 1) and the other class (Class d) will have one end open and one end bridged (structure *4* in Figure 1). Thus, in toto, four classes of bridged polyenes are possible. These four classes are schematically depicted in Figure 1.



$C_NH_{\frac{1}{2}(N+10)}B_{\frac{1}{4}(N-6)}$

1

$C_NH_{\frac{1}{2}(N+2)}B_{\frac{1}{4}(N-2)}$

2

$C_NH_{\frac{1}{2}(N+12)}B_{\frac{1}{4}(N-4)}$

3

$C_NH_{\frac{1}{2}(N+4)}B_{\frac{1}{4}N}$

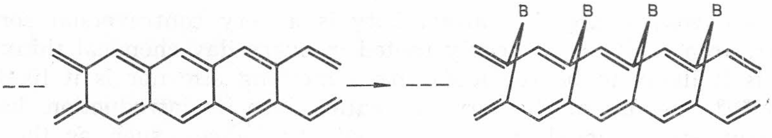
4

Figure 1. Four classes of bridged polyenes

B in Figure 1 symbolizes the bridge fragment. It may be an atom or a group. In the six prepared "hairpin" polyenes the CH_2-group was used as the bridge.[2]

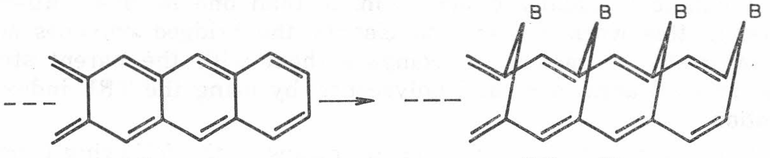
Class c and Class d may also be formally obtained from the bridged annulenes. Class c may be obtained by removing a bond from one end and a —C=C— fragment from the other end. In Class d the end from which the bond is removed is bridged, whilst the other end from which the fragment —C=C— is removed remains open.

There is also another theoretical possibility open for the schematic construction of bridged polyenes. Class a may be generated from linear polyacenes by attaching vinyl fragments to the 2, 3 positions of the end hexagon and by replacing the bonds common to two rings with bridges:



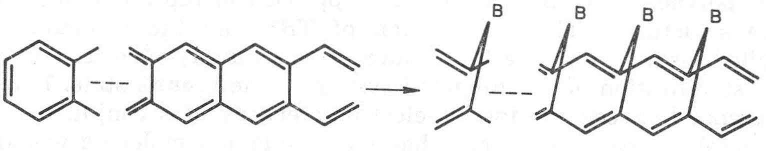
$C_NH_{\frac{1}{2}(N+10)}$ $\qquad$ $C_NH_{\frac{1}{2}(N+10)}B_{\frac{1}{4}(N-6)}$

Class b may be generated from linear polyacenes by replacing the bonds common to two rings and one of the end-bonds parallel to these bonds with bridging groups:



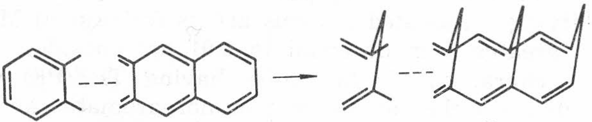
$C_NH_{\frac{1}{2}(N+6)}$ $\qquad$ $C_NH_{\frac{1}{2}(N+2)}B_{\frac{1}{4}(N-2)}$

Class c may be generated from linear polyacenes by attaching vinyl fragments to the 2, 3 positions and by removing the —C=C— fragment from the other end, and then by replacing the bonds common to two rings by bridges:



$C_NH_{\frac{1}{2}(N+6)}$ $\qquad$ $C_NH_{\frac{1}{2}(N+4)}B_{\frac{1}{4}N}$

Finally Class d may be generated from linear polyacenes by replacing the bonds common to two rings and one of the end-bonds parallel to these bonds by bridges whilst the —C=C— fragment is removed from the other end-hexagon:



$C_NH_{\frac{1}{2}(N+6)}$ $\qquad$ $C_NH_{\frac{1}{2}(N+4)}B_{\frac{1}{4}N}$

There are therefore four families of parent structures which may be formally used as precursors for generating bridged polyenes. These are polyenes, bridged annulenes, polyacenes, and polyacenes with vinyl fragments attached at positions 2 and 3, respectively.

OUTLINE OF THE THEORETICAL APPROACH

We have studied the aromatic stabilities of "hairpin" polyenes by means of the topological resonance energy, TRE, approach.[5,6] The same theoretical approach has successfully been used to study aromaticity in bridged annulenes[7] and bridged heteroanulenes,[8] respectively.

We are well aware that aromaticity is a very contraversial concept.[9-11] However, aromaticity is so deeply rooted in every day chemical thinking that neither is it likely to be replaced with something else nor is it likely to be rejected.[12-19] The use of the term aromatic, since its introduction, has never been quantitative, though various aromaticity indices, such as the one we use, may sometimes serve as quantitative criteria for the comparison of different conjugated structures. We use the TRE index as a device for classifying conjugated structures into three very broad groups: aromatic, non-aromatic, and anti-aromatic species. This classification should serve as an indicator to experimental chemists who know from experience that a molecule labelled aromatic is usually easier to make than one labelled anti-aromatic. Therefore, in this work we wish to classify the bridged polyenes according to their aromatic character and compare them with the parent structures: polyenes, bridged annulenes, and polyacenes, by using the TRE index for the classification.

The numerical work is carried out by means of the following formula:[5,6,20]

$$\mathrm{TRE} = \sum_{i=1}^{N} g_i \left(x_i - x_i^{ac}\right) \tag{1}$$

where x_i's are the Hückel eigenvalues, and x_i^{ac}'s are those of the reference (acyclic, matching) polynomial. The g_i is the orbital occupancy number. The reference polynomial is used in the TRE approach to represent the Dewar-like reference structure.[15] The computation of TRE and the computer program are detailed elsewhere.[21] The TRE index may be interpreted as the degree of aromatic stabilization of a conjugated system in the ground state. It represents the difference between the total π-electronic energy of a conjugated molecule and the total π-electronic energy that the conjugated molecule would possess if it were olefinic in nature.

In order to compare molecules of various sizes, TRE is normalized:

$$\mathrm{TRE\,(PE)} = \mathrm{TRE/N} \tag{2}$$

where TRE(PE) denotes TRE per π-electron, whilst N stands for the total number of π-electrons in the conjugated molecule. The threshold TRE(PE) values for classifying conjugated systems are as follows: (i) Molecules having TRE(PE) values greater than or equal to 0.01 are considered to be of prevailing aromatic character, (ii) Molecules having TRE(PE) values between $+\,0.01$ and $-\,0.01$ are either ambivalent or non-aromatic, and (iii) Molecules with TRE(PE) values less than or equal to $-\,0.01$ are viewed as anti-aromatic.

The amount of interaction across the two sides of the bridged polyene is denoted by k and is the crucial parameter in our calculations. We have varied the homoaromatic parameter k from 0.00 to 1.00 in steps of 0.10. As an examples the TRE, as a function of k is plotted in Figure 2 for two illustrative cases.

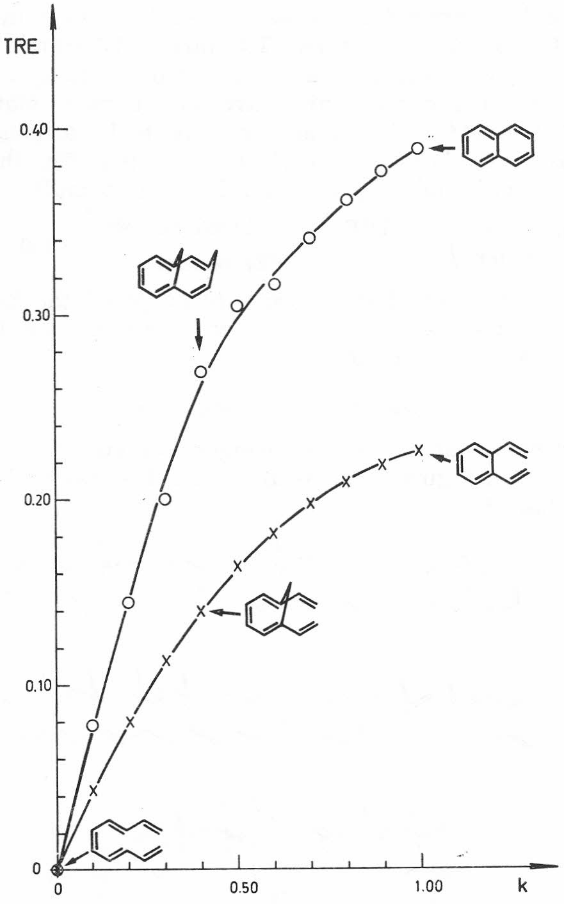


Figure 2. TRE vs. homoconjugative parameter k for bridged [10]polyene

We see that the TRE variation is smooth for molecules ranging from U-shaped [10]polyene to either divinyl-benzene or naphthalene, respectively. Note, TRE (polyene) = 0 by definition.[5] The value of $k = 0.40$ is selected for actual calculations of the TRE index of "hairpin" polyenes and related structures. This value of k has been shown to be quite adequate in our earlier studies on bridged annulenes[7] and bridged heteroannulenes.[8] The same value for the parameter k was used by Dewey et al.[23] in their analysis of spectral data of bridged annulenes. Their work shows that the transannular interaction is rather strong in the bridged structures, i. e. it is about 40% of that between the adjacent $2p_z$ orbitals in benzene. Herndon and Párkányi[24] have also used the same value ($k = 0.40$) in their study on stabilities and properties of bridged annulenes. Apparently, the homoaromatic model of bridged structures with strong 'through-space' interaction across the annulene part at the bridge sites is, in the first approximation, quite reliable for predicting their relative stabilities, reactivities, structural and spectral properties.[7,8,23-31] However, we are quite aware that by assuming that the only effect in operation within the system is the homoaromatic interaction, we have oversimplified the physical picture of the bridged structures. The (aromatic) stability of the bridged structures is probably a result of a complicated interplay of several effects (e. g. conformational, inductive, conjugative, and homoaromatic effects).[32]

Since some people[9,33] think that the only truly aromatic compound is benzene, we have calculated, for each bridged polyene, the percentage of benzene character with the help of the following formula:

$$\%\left(\begin{array}{c}\text{benzene}\\ \text{character}\end{array}\right)=\frac{\text{TRE (PE) (bridged polyene)}}{\text{TRE (PE) (benzene)}}\cdot 100 \qquad (3)$$

where TRE(PE) (benzene) = 0.046.[5] The percentage of the benzene character is, therefore, a measure that determines how close to or how far from benzene aromatic stability a given compounds is.

RESULTS AND DISCUSSION

Schematic representations of the bridged polyenes that were studied in this work are given in Figure 3 (Class a), Figure 4 (Class b), Figure 5 (Class c), and Figure 6 (Class d).

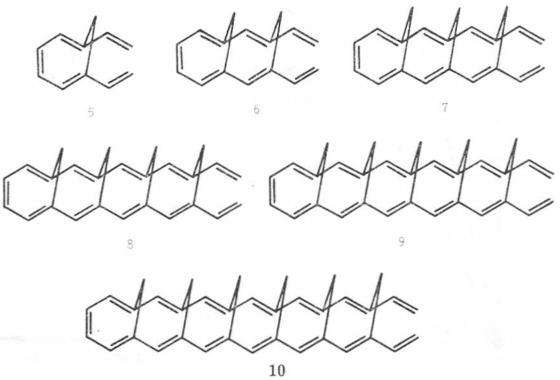


Figure 3. Schematic representation of the lowest bridged polyenes with open ends and with CH_2 bridging groups: Class a, $C_NH_{1/2(N+10)}$ $(CH_2)_{1/4(N-6)}$

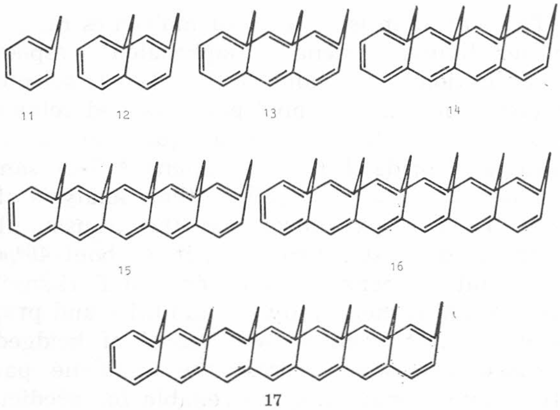
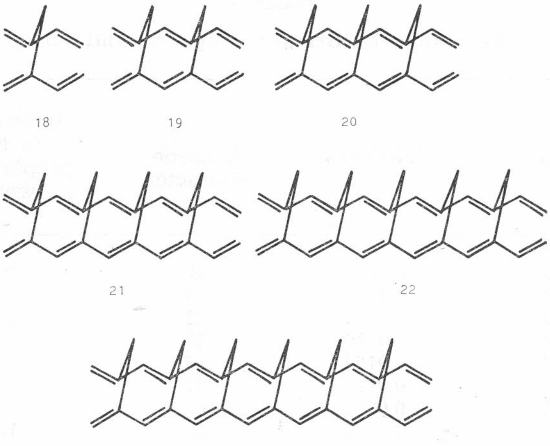


Figure 4. Schematic representation of the lowest bridged polyenes with bridged ends and with CH_2 bridging groups: Class b, $C_NH_{1/2(N+2)}$ $(CH_2)_{1/4(N-2)}$

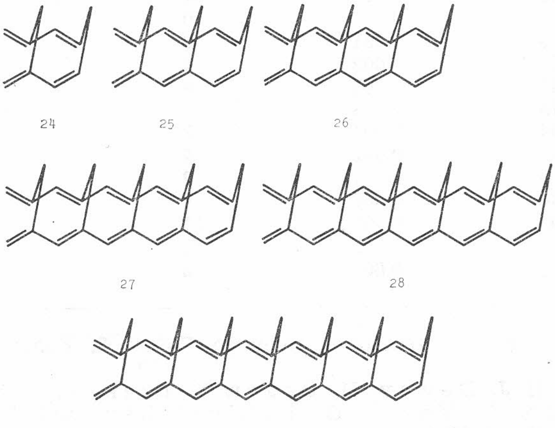


18 19 20

21 22

23

Figure 5. Schematic representation of the lowest bridged polyenes with both ends open and with CH_2 bridging groups: Class c, $C_NH_{1/2(N+12)}\,(CH_2)_{1/4(N-4)}$



24 25 26

27 28

29

Figure 6. Schematic representation of the lowest bridged polyenes with one end open and the other end bridged, and with CH_2 bridging groups Class d,

$$C_NH_{1/2(N+4)}\,(CH_2)_{1/N}$$

The TRE and TRE(PE) values of bridged polyenes from Figure 3, Figure 4, Figure 5, and Figure 6 are given in Table I.

It follows from the results in Table I that the bridged polyenes in Class a and Class b are all aromatic structures, whilst the bridged polyenes in Class c and Class d are all non-aromatic.

The bridged polyenes with bridged ends always possess a greater percentage of benzene character than do the related bridged polyenes with open ends. The meaning of this result is that one more bridge across the polyene sides brings additional stabilization to the structure in comparison to the related structure with an open end. However, both types of the bridged

TABLE I

The TRE and TRE(PE) Indices of Bridged Polyenes and their Benzene Character

»Hairpin« polyene[a]	TRE	TRE(PE)	% of benzene character	Reference to the preparative work
5	0.141	0.0141	31	b
6	0.212	0.0152	33	b
7	0.260	0.0145	32	b
8	0.299	0.0136	30	
9	0.333	0.0128	28	
10	0.370	0.0123	27	
11	0.184	0.0301	67	
12	0.248	0.0248	55	b
13	0.292	0.0209	46	b
14	0.329	0.0183	40	b
15	0.362	0.0164	36	
16	0.393	0.0151	33	
17	0.423	0.0141	31	
18	0	0	0	
19	0.009	0.001	2	
20	0.026	0.002	4	
21	0.049	0.002	4	
22	0.075	0.003	7	
23	0.104	0.004	8	
24	0.013	0.002	4	
25	0.016	0.001	2	
26	0.036	0.002	4	
27	0.093	0.005	11	
28	0.124	0.005	11	
29	0.161	0.006	13	

[a] Numbers correspond to structures given in Figure 3, Figure 4, Figure 5, and Figure 6.

[b] W. Frolich, H. J. Dewey, H. Deger, B. Dick, K. A. Klingensmith, W. Puttmann, E. Vogel, G. Hohlneicher, and J. Michl, *J. Am. Chem. Soc.* **105** (1983) 6211.

polyenes (bridged polyenes with bridged ends, and bridged polyenes with open ends) apparently converge to a situation where there is no difference between them: TRE(PE) [Class a] $\approx$ TRE(PE) [Class b] and TRE(PE) [Class c] $\approx$ TRE(PE) [Class d], respectively. This would happen if both types of structures were to become very large.

The hairpin polyenes with open ends are also expected, just because of the presence of vinyl fragments, to be more reactive than those with bridged ends.

Several of the bridged polyenes in Class b considered here have also been studied by Herndon and Párkányi.[24] These are structures *11, 12,* and *13* in Figure 4. The Herndon-Párkányi RE indices (in eV) for these molecules are 0.18(*11*), 0.33(*12*), and 0.47(*13*). Their RE indices were calculated by means of the following formula:[34]

$$\mathrm{RE} = A \ln (\mathrm{SC}) \qquad (4)$$

where SC is the structure count for a given bridged polyene, whilst A is the least-squares parameter determined on the randomly selected set of conjugated structures ($A = 1.19$).[35] However, they selected a different value for the homoconjugative interaction in the bridged polyenes ($k' = 0.16$). The reasoning behind this choice of parameter k was that the bridged polyenes are more flexible structures than bridged annulenes. The normalized values of their RE indices: 0.030(*11*), 0.033(*12*), and 0.034(*13*), do not make any practical difference between these three molecules. This is in disagreement with our stability prediction based on the TRE(PE) values: $11 > 12 > 13$. The experimental fact is that all three compounds are prepared without any particular difficulty. However, cycloheptatriene (*11*) has been known for a long time,[36] whilst bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene (*12*) and tricyclo[9.4.1.$1^{3,9}$] heptadeca-2,4,7,9,11,13,15-heptaene (*13*) are only recent products of the Cologne-style synthetic chemistry.[3,4] Their preparation was carried out under an inert (argon) atmosphere.

Let us now see how the bridged polyenes compare with the bridged annulenes. The TRE and TRE(PE) values of the bridged annulenes, taken from our earlier work,[7] are reported in Table II. In this table we also give the results obtained by Herndon and Párkányi[24] using their structure-resonance approach and formula (4).

TABLE II

The TRE, TRE(PE), and RE Values of the Bridged Annulenes

Bridged [N] annulene	TRE[a] (β)	TRE(PE)[a] (β)	RE[b] (eV)	Reference to the preparative work
[10]	0.291	0.029	1.04	c
[14]	0.320	0.023	1.23	d
[18]	0.350	0.019	1.38	e
[22]	0.382	0.017		f
[26]	0.425	0.016		
[30]	0.469	0.016		

[a] A. Sabljić, N. Trinajstić, *J. Org. Chem.* **46** (1981) 3457.
[b] W. C. Herndon, C. Párkányi, *Tetrahedron* **38** (1982) 2551.
[c] E. Vogel, H. D. Roth, *Angew. Chem. Int. Edit. English* **3** (1964) 228.
[d] E. Vogel, J. Sombrock, W. Wagemann, *Angew. Chem.* **87** (1975) 591.
[e] W. Wagemann, M. Iyoda, H. M. Deger, J. Sombrock, E. Vogel, *Angew. Chem* **90** (1978) 988.
[f] E. Vogel, in: *Current Trends in Organic Synthesis*, Edited by H. Nazaki, Pergamon, Oxford, 1983, p. 379.

Bridged [N]annulenes in Table II are all predicted to be aromatic structures. This prediction agrees with the reports on the preparation and properties of the bridged annulenes by Vogel and the Cologne group.[3,4,37–42] The bridged[10]-, [14]-, [18]- and [22]annulene have all been prepared[3,4,37,40,41] whilst the bridged [26]- and [30]annulene are not yet known. There are increasing difficulties in preparing the higher bridged [N]annulenes.[4] These are due to the synthetic methodology and need not be tied only to the aromatic properties of these compounds. The bridged annulenes appear to be more stable than the corresponding hairpin polyenes of both types:

$$\text{Polyenes} < \text{Bridged polyenes} < \text{Bridged annulenes} \qquad (5)$$

It has already been pointed out that the bridged annulenes are more stable than the related annulenes, but less stable than the corresponding linear polyacenes:[7]

$$\text{Annulenes} < \text{Bridged annulenes} < \text{Polyacenes} \qquad (6)$$

The same relationship also holds for heteroannulenes, bridged heteroannulenes and heteropolycycles:

$$\text{Heteroannulenes} < \text{Bridged heteroannulenes} < \text{Heteropolycycles} \qquad (7)$$

Now, the relationships (5) and (6) may be combined to give the stability order for all structures considered:

$$\begin{aligned}[\text{N}]\text{polyenes} < [\text{N}]\text{annulenes} < \text{Bridged } [\text{N}]\text{polyenes} <\\ < \text{Bridged } [\text{N}]\text{annulenes} < \text{Polyacenes} \qquad (8)\end{aligned}$$

Note, that in the above $N = 4n + 2$ ($n = 1, 2, 3, \ldots$).

The above stability order is generally obeyed. There is an exception only in one case, that is in the case of [10]annulene, because its TRE(PE) value (0.016)[7] is slightly greater than the TRE(PE) value (0.014) for the corresponding bridged [10]polyene with the open end. However, the TRE(PE) value of [10]annulene is much lower than the TRE(PE) value (0.025) of the corresponding bridged [10]annulene with the bridged end.

PREDICTION FOR UNKNOWN BRIDGED POLYENES

We now wish to mention briefly our studies on other possible bridged polyenes.

(a) Bridged Polyenes with Asymmetric Bridges

We will first treat bridged polyenes in which the bridges are symmetrically placed. We will consider all kinds of such bridged polyenes. In some cases all bridges are placed asymmetrically, whilst in some structures the bridges are placed both symmetrically and asymmetrically. Some such polyenes have open ends and some have bridged ends. Representative classes of this kind of bridged polyenes are shown in Figure 7.

TRE and TRE(PE) values for the bridged structures in Figure 7 are as follows: *30*: 0.092 (0.007), *31*: 0.028 (0.002), *32*: 0.180 (0.013), and *33*: 0.095 (0.007). TRE(PE) values are given in the brackets.

In all cases studied the bridged polyenes with asymmetric bridges are always predicted to be less aromatic than the corresponding bridged polyenes with symmetric bridges. For example, compare *6* with *30* and *31*. Whilst the TRE(PE) value of *6* indicates that this molecule is aromatic the TRE(PE) values of *30* and *31* suggest that both structures are non-aromatic. Similarly, *13* is predicted to be more stable than the corresponding bridged polyenes with asymmetric bridges *32* and *33*. Therefore, placing the bridge asymmetrically causes destabilization of the bridged structure. A similar observation has already been made in the case of bridged annulenes.[7] The destabilization effect of an asymmetrically placed bridge is attributed to the fact that in

(a) Hairpin polyene with an asymmetric bridge and the open end

30

(b) Hairpin polyene with all asymmetric bridges and the open end

31

(c) Hairpin polyene with an asymmetric bridge and the bridged end

32

(d) Hairpin polyene with all bridges placed asymmetricall, but one which bridges the end

33

Figure 7. The representative structures for bridged polyenes with asymmetric bridges (broken lines denote the positions of the bridges)

this case two atoms of the same parity (same colour) are connected. When the bridge is placed symmetrically it connects two atoms of different parity (different colour). This is illustrated in Figure 8. According to the PMO arguments the interaction between the positions of different parity is stabilizing, whilst in the opposite case (i. e. the interaction between the positions of same parity) it is destabilizing.[43,44]

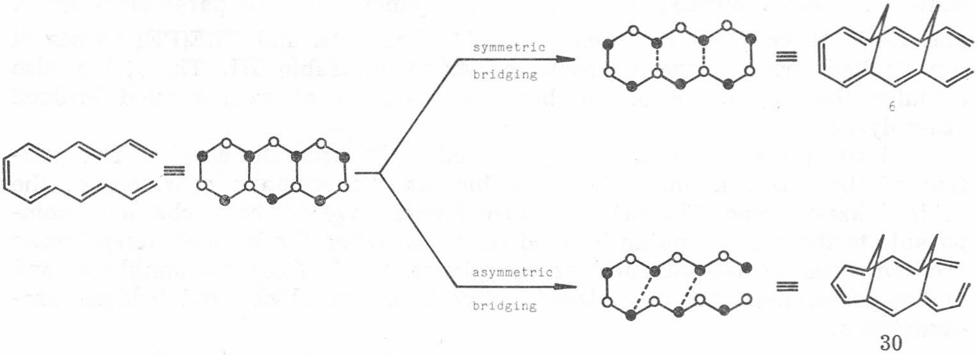


Figure 8. Illustrative case for placing bridges symmetrically and asymmetrically on the U-shaped polyene

(b) Bridged Aza-Polyenes

Secondly we have studied the bridged aza-polyenes. There is no reason why aza-polyenes could not be bridged.[45] The nitrogen atom may be placed in any position, except at the bridging sites. We have considered all kinds of bridged aza-polyenes (with and without bridged ends). The bridged polyenes that were studied are given in Figure 9.

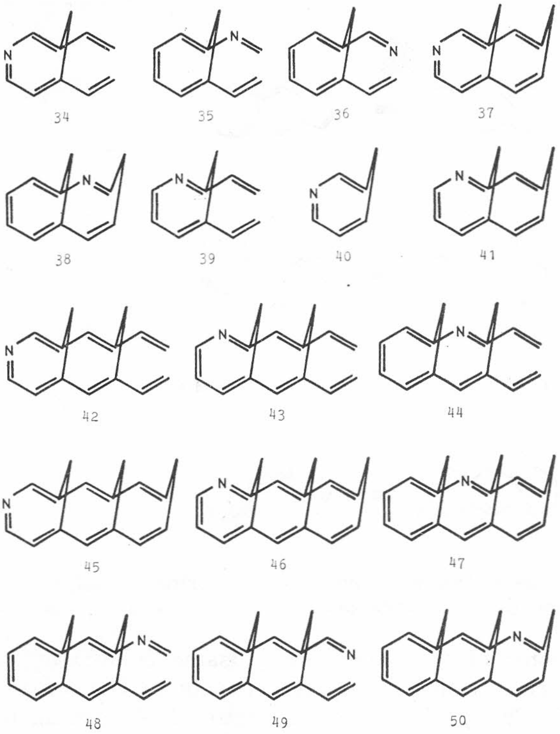


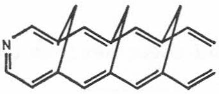
Figure 9. to be continued

The TRE calculation for bridged aza-polyenes have been carried out in the standard manner already described in the paper with the parameters for $\dot{N}$ and C—$\dot{N}$ taken from Hess and Schaad.[46] The TRE and TRE(PE) values of the studied bridged aza-polyenes are given in Table III. This table also contains the percentage of the benzene character of each studied bridged aza-polyene.

All studied aza-polyenes are predicted to be aromatic species. The position of the nitrogen only slightly influences the aromatic character of the bridged aza-polyene. The bridged aza-polyenes have aromatic character comparable to the corresponding bridged polyenes. When the bridged aza-polyenes are compared to aza-polyenes, aza-annulenes, the bridged aza-annulenes and to aza-polyacenes, they are placed between aza-annulenes and bridged aza-annulenes:

$$\text{Aza-polyenes} < \text{aza-annulenes} < \text{bridged aza-polyenes} < \text{bridged aza-annulenes} < \text{aza-polyacenes} \qquad (9)$$

Figure 9. continued



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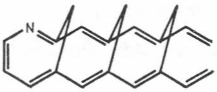

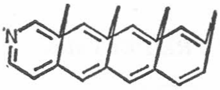

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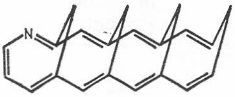

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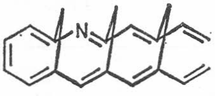

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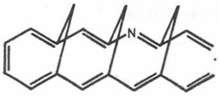

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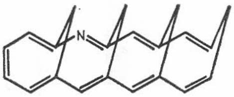

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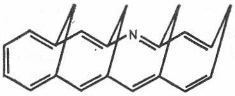

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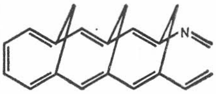

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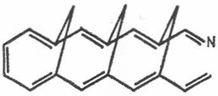

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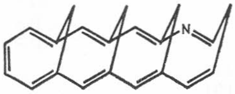

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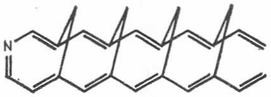

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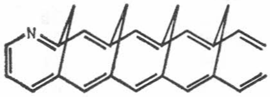

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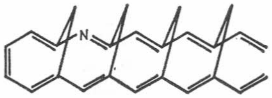

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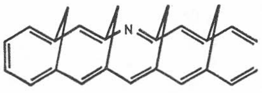

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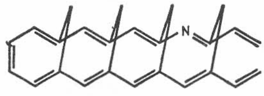

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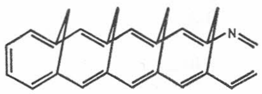

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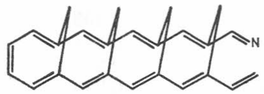

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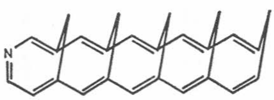

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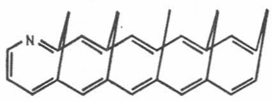

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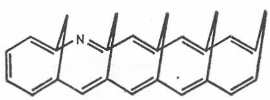

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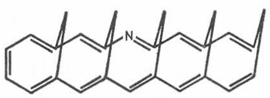

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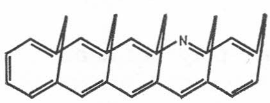

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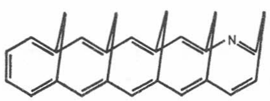

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Figure 9. Schematic representation of the studied bridged aza-polyenes

TABLE III

The TRE and TRE(PE) Values of Bridged Aza-Polyenes and their Benzene Character

Bridged aza-polyene[a]	TRE	TRE(PE)	% of benzene character
34	0.119	0.012	26
35	0.146	0.014	32
36	0.125	0.013	28
37	0.203	0.020	45
38	0.238	0.024	52
39	0.084	0.008	18
40	0.151	0.025	55
41	0.188	0.019	41
42	0.182	0.013	29
43	0.182	0.013	29
44	0.204	0.015	32
45	0.249	0.018	39
46	0.250	0.018	39
47	0.204	0.015	32
48	0.215	0.015	34
49	0.191	0.014	30
50	0.274	0.020	43
51	0.233	0.013	29
52	0.235	0.013	29
53	0.291	0.016	36
54	0.274	0.016	36
55	0.252	0.014	31
56	0.257	0.014	31
57	0.311	0.017	38
58	0.316	0.018	39
59	0.261	0.015	32
60	0.242	0.013	30
61	0.311	0.017	38
62	0.273	0.012	27
63	0.275	0.013	28
64	0.293	0.013	29
65	0.258	0.012	26
66	0.261	0.012	26
67	0.265	0.012	26
68	0.249	0.011	25
69	0.326	0.015	33
70	0.328	0.015	33
71	0.347	0.016	35
72	0.312	0.014	31
73	0.314	0.014	31
74	0.308	0.014	31

[a] Numbers correspond to structures given in Figure 8.

However, it should be noted that the bridged aza-polyenes with open ends are very close in their aromatic character to aza-annulenes, whilst the bridged aza-polyenes with bridged ends are rather close to the bridged aza-annulenes, respectively.

Our prediction is that the bridged aza-polyenes should be comparable in their aromatic character to the bridged polyenes. Perhaps the same synthetic strategy as one used for the preparation of the bridged polyenes may also be employed for preparing the bridged aza-polyenes. We would not be surprised if such an approach is not already in use by the Cologne Group. After all, they have already made a derivative of the bridged aza-polyene (6-vinyl--1-cycloheptatrienylisocyanate), but with the different aim.[3]

CONCLUSIONS

According to the TRE model, the bridged polyenes (and bridged aza--polyenes) are aromatic structures. The bridged polyenes with an open end are less aromatic than the corresponding bridged polyenes with a bridged end. The bridged polyenes with both open ends and with one open end and one bridged end are predicted to be non-aromatic species. The bridged aza--polyenes are of comparable aromatic character to bridged polyenes. Since the TRE model has been used previously to study annulenes (and aza-annulenes), bridged annulenes (and bridged aza-annulenes), and polyacenes (and aza-polyacenes), we could compare the aromatic character of these structures to that predicted for the bridged polyenes (and bridged aza-polyenes). It has been found that the bridged polyenes (bridged aza-polyenes) are placed according to their aromatic character between annulenes (aza-annulenes) and bridged annulenes (bridged aza-annulenes), respectively. The available experimental evidence supports this result.

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SAŽETAK

Aromatska stabilnost premoštenih poliena

Albin Jurić, Nenad Trinajstić i Gani Jashari

Studirana je aromatska stabilnost premoštenih poliena s pomoću topologijske rezonancijske energije. Teorijska je aromatska stabilnost premoštenih poliena uspoređena s aromatskom stabilnošću poliena, anulena, premoštenih anulena i poliacena. Ta je usporedba pokazala da postoji slijedeći redoslijed između spomenutih klasa konjugiranih molekula (aromatičnost raste od lijeva na desno):

polieni < anuleni < premošteni polieni < premošteni anuleni < poliaceni.

Postojeći eksperimentalni podaci u skladu su s gornjim redoslijedom.