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ON THE AROMATIC STABILITY OF AZULENOFURANS, AZULENOPYRROLES AND AZULENOTHIOPHENES

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Abstract - The aromatic stabilities of isomeric azulenofurans, azulenopyrroles and azulenothiophenes have been studied by three theoretical models of aromaticity: the graphical model, the conjugated circuits model and the topological resonance energy model. All three models predict that molecules with the delocalized underlying carbon structure are more stable than those with the quinoid structure. In each class of positional isomers, azulenopyrroles are always predicted to be more stable than the corresponding isomeric azulenothiophenes, and these more stable than the corresponding azulenofurans. However, all azulenofurans, azulenopyrroles and *azulenothiophenes* are predicted to be less aromatic than the parent hydrocarbon 2,3-benzazulene.

It is suggested that the differences in stability between azulenofurans, azulenopyrroles and azulenothiophenes is related to the differences in stability between the heterocyclic parts of the molecules, i.e. furan, pyrrole and thiophene, since the carbon parts are identical.

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Recently the preparation of azulenofurans, azulenopyrroles and azulenothiophenes have been reported.[1-4] Azulenofurans, azulenopyrroles and azulenothiophenes are tricyclic unsaturated compounds containing a terminal five-membered heterocycle (furan, pyrrole and thiophene). Their physical properties and chemical behaviour are of current interest.[4] Some of these compounds and their derivatives may also possess biologically interesting properties. Here we wish to report our study of their aromatic stabilities.

Diagrams of isomeric azulenofurans, azulenopyrroles and azulenothiophenes are given in Figure 1.

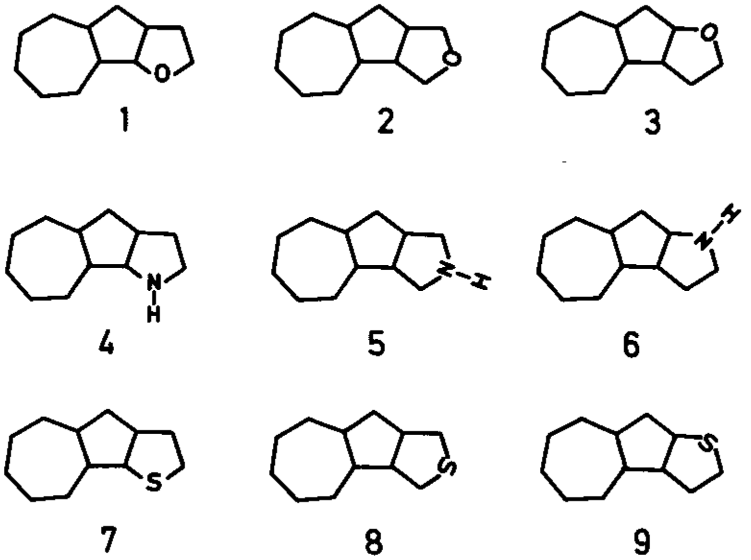

Fig. 1. Diagrams of isomeric azulenofurans, azulenopyrroles and azulenothiophenes

The structures in Figure 1 can be partitioned into three classes of positional isomers; i.e., into three classes of structural isomers which differ in the position of the heteroatom.[5] The generalized schematical representation of these three classes of positional isomers is given in Figure 2.

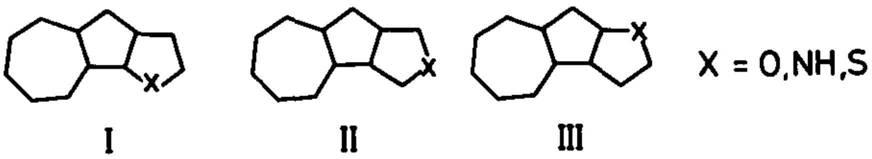

Fig. 2. The generalized schematical representation of structures given in Figure 1 as partitioned into three classes of positional isomers. The symbol X stands for O, NH or S.

Each class of these positional isomers possesses a common carbon skeleton. These skeletons are given in Figure 3. They may simply be obtained by the removal of the heteroatom and the adjacent bonds from the parent structure.

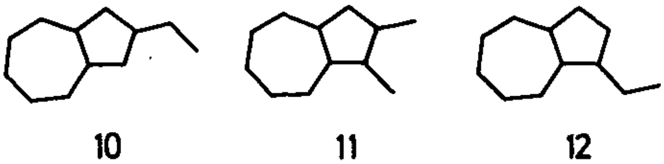

Fig. 3. Diagrams of the carbon skeletons corresponding to each class of positional isomers depicted schematically in Figure 2.

Azulenofurans, azulenopyrroles and azulenothiophenes are structures isoelectronic with 2,3-benzazulene. The diagram of 2,3-benzazulene is given in Figure 4.

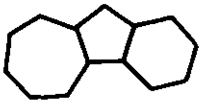

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Fig. 4. The diagram of 2,3-benzazulene

2,3-Benzazulene possesses three Kekulé structures. These are given in Figure 5. Kekulé structures of 2,3-benzazulene may be used for formal generation of azulenofurans, azulenopyrroles and azulenothiophenes by replacing the -HC=CH- fragment with -X- (X = O, NH, S). Kekulé structures A and C of 2,3-benzazulene (see Figure 5) lead to isomers I and III, whilst Kekulé structure B leads to isomers of type II. This is shown in Figure 6.

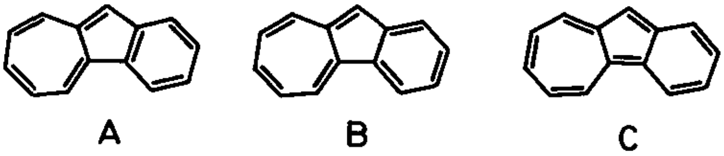
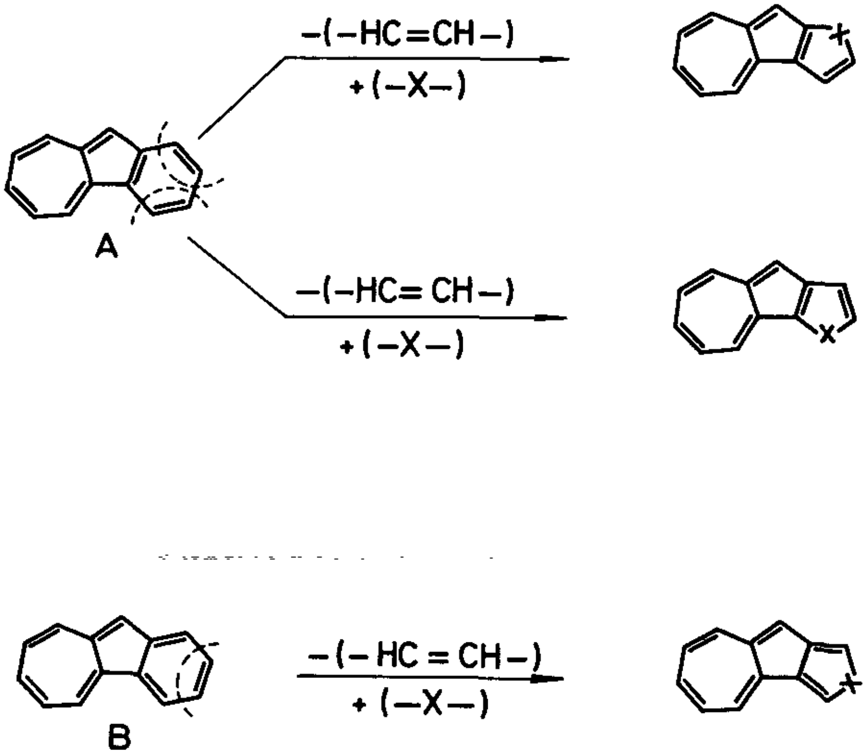


Fig. 5. Kekulé structures belonging to 2,3-benzazulene



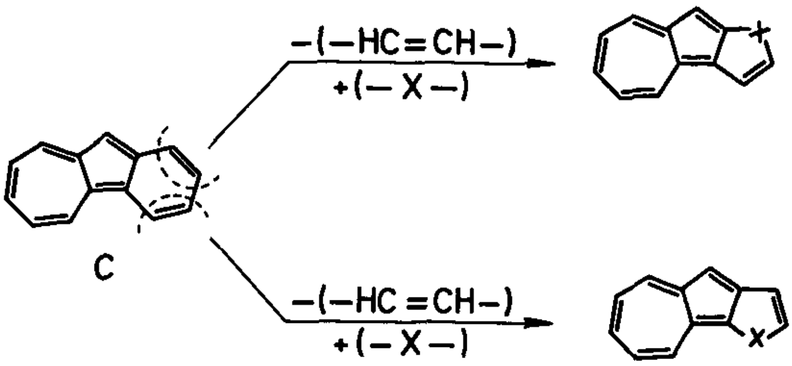


Fig. 6. The generation of azulenofurans, azulenopyrroles or azulenothiophenes from the parent hydrocarbon 2,3-benzazulene

We have studied the aromatic stabilities of azulenofurans, azulenopyrroles and azulenothiophenes by means of three theoretical models of aromaticity. The first model, the so-called graphical model, is based on the consideration of the aromatic stabilities of the underlying carbon skeletons and the predictions obtained for them are then used for predicting the stabilities of the structures as a whole.[6,7] The second model considered is the conjugated circuit model.[8-10] The essence of this model is the enumeration of conjugated circuits that are contained in each Kekulé structure of the conjugated molecule. The resonance energy is then calculated by the following expression:[9,11]

$$RE = \frac{1}{K} \sum_{n \geq 1} (a_n R_n + b_n Q_n + c_n X'_n + d_n X''_n) \qquad (1)$$

where K is the number of Kekulé structures of the molecule, R_n and Q_n are the parametric values for conjugated circuits of size 4n + 2 and 4n (n = 1, 2,...), respectively, and X'_n and X''_n are the parametric values for conjugated circuits containing the heteroatom X of size 4n + 2 and 4n, respectively, whilst a_n, b_n, c_n and d_n are the numbers of R_n, Q_n, X'_n and X''_n circuits. In the numerical work we will consider only conjugated circuits of size n = 14 or less. In doing this we follow the suggestion of Herndon[12] according to which only the smallest circuits have appreciable contributions to the molecular aromatic stability.

The parameters needed for calculating the REs with the conjugated circuits model are taken from Randić et al.[8-10,13,14]

The third theoretical model of aromaticity used is the topological resonance energy (TRE) approach.[15-17] TRE of a conjugated molecule can be calculated using the following formula:

$$TRE = \sum_{i=1}^{N} g_i (x_i - x_i^{ac}) \qquad (2)$$

where x_i's *are the* Hückel *eigenvalues*, whilst x_i^{ac}'s are those of the reference polynomial. The g_i is the orbital occupancy number. The reference polynomial used in the TRE model represents the Dewar-type acyclic reference structure.[18] The TRE index may be interpreted as the degree of aromatic stabilization of a (poly)cyclic conjugated system in the ground state. It represents the difference between the total π electron energy of a conjugated molecule and the total π electron energy that the conjugated molecule would possess if it were olefinic in nature.

RESULTS AND DISCUSSION

(i) The graphical model

The stabilities of structures 10, 11 and 12 are related to their Kekulé structure counts:

10 (K = 2) ≈ 12 (K = 2) > 11 (K = 1)

The above result leads immediately to the aromatic stability prediction for the systems I, II and III:

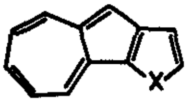
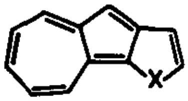
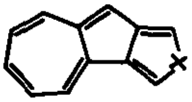
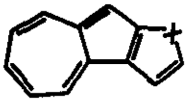
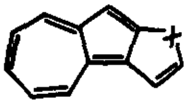
$$I \approx III > II \qquad (3)$$

This result is in agreement with many experimental observations that heterocycles with the quinoid underlying carbon structure (system II in our case) are less stable than those with the delocalized underlying carbon structure (*systems* I *and* III) when they contain only 4n + 2 rings.[20-24]

(ii) The conjugated circuits model

The conjugated circuits counts for systems I, II and III are shown in Table 1.

Table 1. The conjugated circuits for heterocyclic systems in Figure 2

Heterocyclic systems	Kekulé structure	Conjugated circuits
I		$R_2 + X_1$
		$R_2 + X_3$
II		$X_1 + X_3$
III		$R_2 + X_1$
		$R_2 + X_3$

The following are their RE expressions:

$$RE(I) = (2R_2 + X_1 + X_3)/2 \quad (4)$$

$$RE(II) = X_1 + X_3 \quad (5)$$

$$RE(III) = (2R_2 + X_1 + X_3)/2 \quad (6)$$

We can predict the relative aromatic stabilities of systems I-III by considering only their RE expressions. The prediction is the same as the above (3).

The RE expression for the parent hydrocarbon 2,3-benzazulene is given by:

$$RE\ (\underline{13}) = (2R_1 + 2R_2 + 2R_3)/3 \qquad (7)$$

Comparison of the RE expressions (4)-(7) leads to the conclusion that the parent hydrocarbon 13 should be more stable than any of the daughter systems. Some experimental evidence is supportive of the above prediction.[25]

However, if we wish to carry out numerical work we need to use the parametric values for the conjugated circuits. These are given in Table 2.

Table 2. The parametric values for conjugated circuits.

Conjugated circuit	Parametric values[a] (eV)[b]
R_1	0.869
R_2	0.247
R_3	0.100
O_1	0.069
O_2	0.020
O_3	0.008
N_1	0.370
N_2	0.105
N_3	0.043
S_1	0.282
S_2	0.130
S_3	0.032

(a) Taken from Refs. 8, 11, 13, 14.

(b) The conversion from eV's to J's is given by: 1 eV = $1.6021892 \times 10^{-19}$ J.

The REs in terms of conjugated circuits for molecules 1 - 9 and 13 are given in Table 3.

The results in Table 3 confirm earlier qualitative predictions that molecules with structures corresponding to systems I and III are of comparable aromatic stabilities whilst molecules corresponding to system II are much less stable. However, the results in Table 3 allows one to compare molecules 1 - 9 amongst themselves, and to the parent molecule 13.

Table 3. The RE expressions and REs of molecules 1 - 9 and 13

Molecule[a]	RE expression[b]	RE		Reference to the preparatory work
		In terms of R_1[c]	Numerical value (eV)	
1	$(2R_2 + O_1 + O_3)/2$	0.328	0.285	4
2	$O_1 + O_3$	0.088	0.076	-
3	$(2R_2 + O_1 + O_3)/2$	0.328	0.285	1
4	$(2R_2 + N_1 + N_3)/2$	0.522	0.453	4
5	$N_1 + N_3$	0.475	0.413	1
6	$(2R_2 + N_1 + N_3)/2$	0.522	0.453	1
7	$(2R_2 + S_1 + S_3)/2$	0.465	0.404	3
8	$S_1 + S_3$	0.362	0.315	3
9	$(2R_2 + S_1 + S_3)/2$	0.465	0.404	2
13	$(2R_1 + 2R_2 + 2R_3)/3$	0.933	0.810	25

(a) Diagrams of the studied molecules are given in Fig. 1 and Fig. 4.

(b) The RE expressions contain only circuits of size 14 or less.

(c) $R_2 = 0.284R_1$; $R_3 = 0.115R_1$; $O_1 = 0.079R_1$; $O_3 = 0.009R_1$; $N_1 = 0.426R_1$; $N_3 = 0.049R_1$; $S_1 = 0.325R_1$; $S_3 = 0.037R_1$.

The following aromatic stability order for each class of positional isomers is established:

Class I : $4 > 7 > 1$ (8)
Class II : $5 > 8 > 2$ (9)
Class III: $6 > 9 > 3$ (10)

We can also order all molecules studied in Table 3 according to their RE indices. The stability order is given below:

$$13 > 4 \approx 6 > 7 \approx 9 > 5 > 1 \approx 3 \approx 8 > 2 \qquad (11)$$

It appears that all these molecules or their derivatives are known except azuleno(1,2-c)furan (2).

(iii) The TRE model

The TREs are calculated according to formula (2). The values of parameters for >O:, >N̈H and >S: are taken from Hess and Schaad.[26,27] The numerical values of the TREs are given in Table 4.

Table 4. The TRE values for molecules 1 - 9 and 13

Molecule[a]	TRE
1	0.153
2	0.062
3	0.150
4	0.198
5	0.183
6	0.204
7	0.184
8	0.158
9	0.188
13	0.287

(a) Diagrams of the studied molecules are given in Fig. 1 and Fig. 4.

The results from Table 4 once again predict that the delocalized structures (positional isomers belonging to systems I and III) are more stable than the quinoid (localized) structure (positional isomers belonging to system II). However, the difference between isomers I and III, and isomer II vary in magnitude on going from azulenofurans (where the difference is the largest) to azulenopyrroles (where the difference is the smallest) and azulenothiophenes (where the difference is in between the above two classes). Azulenofurans, azulenopyrroles and azulenothiophenes are again predicted to be less aromatic than the parent hydrocarbon 2,3-benzazulene. Finally, the TRE values lead to the following stability order:

$$\underline{13} > \underline{4} \approx \underline{6} > \underline{5} \approx \underline{7} \approx \underline{9} > \underline{1} \approx \underline{3} \approx \underline{8} > \underline{2}. \qquad (12)$$

The only difference between this ordering and the one given earlier (11) is in the position of structure 5 which is now placed together with 7 and 9, whilst earlier 5 was predicted to be slightly less aromatic than 7 and 9.

(iv) *The origin of the differences between azulenofurans, azulenopyrroles and azulenothiophenes*

The differences between isomeric azulenofurans, azulenopyrroles and azulenothiophenes are related to the differences in the stability of the heterocyclic part of the molecule, because the carbon part is identical in all structures within the same class (see Fig. 2 and Fig. 3).

Within each class of the positional isomers RE (conjugated circuits) and TRE values predict the distributions (8), (9) and (10). In all three cases the most stable are isomeric azulenopyrroles, then azulenothiophenes and finally the least stable are azulenofurans. The same stability order is found for furan, pyrrole and thiophene:[5]

$$\text{pyrrole} > \text{thiophene} > \text{furan}. \qquad (13)$$

Various theoretical aromaticity indices support the above: usually predicting pyrrole and thiophene to be aromatic and furan to be a non-aromatic structure. Therefore the difference in the aromaticity of the tricyclic heterosystems studied here should be essentially the same as those of the corresponding five-membered heterocycles.

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