Resonance Energy as a Criterion for Reactivities of Conjugated Hydrocarbons*

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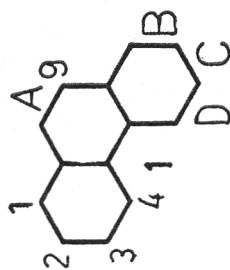
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A simple method based on a topological resonance energy index is proposed for predicting the reactivities of conjugated hydrocarbons. In comparison with other simple methods introduced (*e. g.*, the Kekulé structure count method[1]) it embraces both alternant and non-alternant hydrocarbons without additional adjustment of the theory.
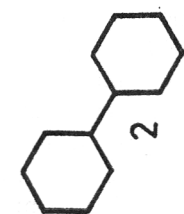
The recently introduced topological definition of resonance energy[2], based on the earlier Dewar proposal[3] according to which a polyene reference structure instead of the ethylene reference structure should be used in the resonance energy calculations, has enabled us to study the aromatic stability of various conjugated molecules[4]. Now we wish to report how one may predict the most probable position in a conjugated molecule towards an addition or substitution reaction using the topological resonance energy (per electron), *TRE(PE)*, values[5] only. For example, there are four different bonds in the phenanthrene molecule (1) where the reaction of addition may occur and thus, the four different π-electron networks should be considered, (2)—(5) (see Figure). The *TRE(PE)* values of phenanthrene and of the four π-electron subsystems are given in the Figure below each structure considered. It should be noted that the compound is considered aromatic if its *TRE(PE)* > 0, otherwise it is nonaromatic *(TRE(PE) = 0)* or antiaromatic *(TRE(PE) $<$ 0)*. Considering the aromaticity of π-networks (1)—(5) one can see that only the addition to bond A of the phenanthrene molecule leads to the more stable π-electron structure (2) while addition to bonds B, C, and D produces less stable π-electron systems in regard to phenanthrene as a reference structure. It can be concluded that the reactivity towards addition of phenanthrene bonds decreases in the order A $\gg$ B $=$ C $>$ D and this agrees with the experimental observation that in most cases the addition reaction occurs at bond A[6,7].

The electrophilic substitution on a certain aromatic molecule may be connected with the stability of the π-electron fragment in the transition state, which is supposed to involve a sp³ hybridized carbon atom with a localized electron pair taken from the π-electron system[8]. There are five topologically different carbon atoms in phenanthrene in respect to the substitution reaction and as the result there are five different π-electron fragments possible carrying
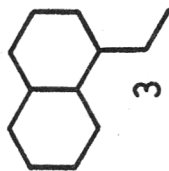

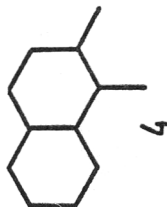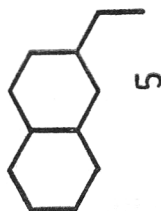* Contribution No. 191 of the Laboratory of Physical Chemistry.

5   0.030

10   0.026

15   0.023

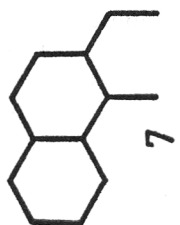4   0.021

9   0.024

14   0.034

3   0.031

8   0.020

13   0.014

2   0.042

7   0.021

12   0.021

A B C D
9 1
1 4
2 3   0.039

6   0.023

11   0.039

21 0.001
(0.001)

20 0.025
(—0.048)

19 0.000
(0.000)

18 0.023

17 0.030

16 0.019

27 —0.004

26 —0.095

25 0.001

24 —0.018

23 —0.028
(0.024)

22 —0.060
(0.023)

30 —0.015

29 0.000

28 —0.009
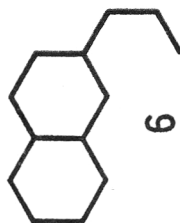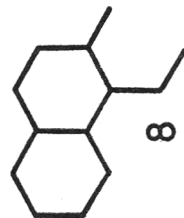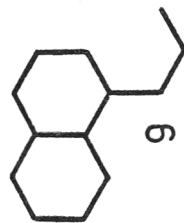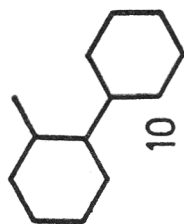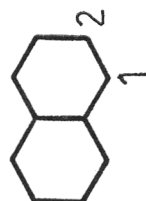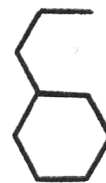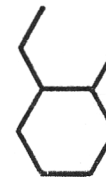
Figure.
π-electron skeletons of the molecules under consideration. TRE(per eleetron) values (in β units) are given below each structure for positively charged substrates in electrophilic substitution reactions. Number in brackets under the azulene fragments represent TRE(per electron) values (in β units) for negatively charged species related to nucleophilic substitutions.

a positive charge, (6)—(10), in the transition state. We have calculated the aromatic stability of these cations and concluded that the m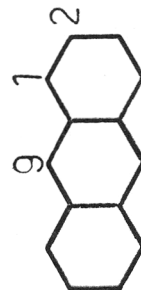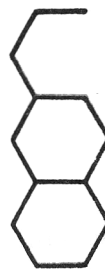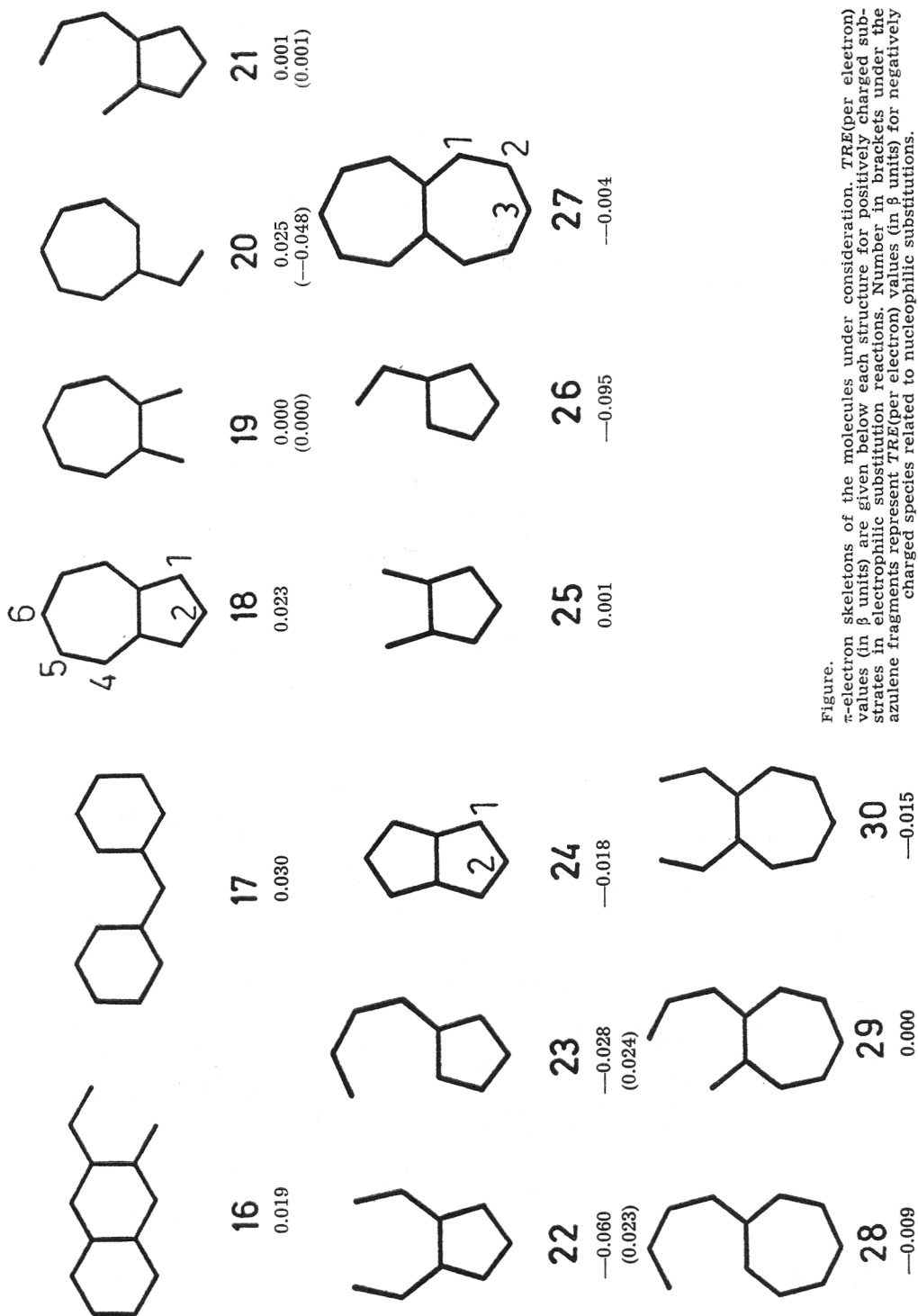ost aromatic one can be ascribed to the most preffered transition state; that is to the transition state with atom 9 as the position of a substitution reaction[9,10]. Note that there are no great differences between phenanthrene atoms, as it is the case for naphthalene molecule, (11)—(13), where atom 1 is much more preferred for electrophilic substitution than atom 2 [9,11]. The same applies to the anthracene molecule (14): electrophilic substitution at position 9 includes stable transition state species carbonium ion (17)[12].

In addition, the nonalternant molecules may be taken into account in the same way. Here we see the advantage of our method in comparison with some other simple approaches (e. g. the Kekulé structure count[1]) which may be limited to alternant systems only. Azulene (18), pentalene (24), and heptalene (27) are taken as test examples. There are five non-equivalent carbon atoms in the azulene molecule which can undergo substitution reactions. The corresponding π-electron fragments are (19), (20), (21), (22), and (23). The most stable one is (20). This is in agreement with Anderson's result which have provided the unequivocal evidence that azulene undergoes electrophilic substitution in 1-position[13].

Structure (25) is predicted to be the most stable when an electrophilic attack towards the pentalene molecule is considered while this is the case for structure (29) when the heptalene molecule is considered.

It is very interesting to see how our method distinguishes between two rings in the azulene molecule. The numerical results indicate that an electrophilic attack towards seven-membered ring is an unfavourable one but when one estimates the probability of a nucleophilic attack the findings are quite opposite. We have found position 4 (the corresponding structure is (23)) to be the most likely to undergo a nucleophilic reaction. This result finds its confirmation in an earlier experimental study[14]. Positions 2 and 5 are nearly equally suitable for both kind of substitution reactions but the corresponding transition state species are nonaromatic. The above results permit the conclusion that there is an electron dislocation from the seven to the five-membered ring of the azulene molecule which is in accord with the earlier theoretical[15] and experimental[13] results.

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SAŽETAK

Rezonancijska energija kao kriterij reaktivnosti konjugiranih ugljikovodika

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Predložena je jednostavna metoda za predviđanje reaktivnosti konjugiranih ugljikovodika. Temelji se na indeksu topološke rezonancijske energije. Ova metoda obuhvaća svojstva kako alternantnih, tako i nealternantnih ugljikovodika bez dodatne parametrizacije.

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