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Topological Resonance Energies of Annulenes*

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The recently developed concept of topological resonance energy, *TRE*, (the optimal non-parametric realization of Dewars-type resonance energy, *DRE*) is applied to neutral (odd and even) and charged annulenes. Analytical expressions for *TRE* of neutral annulenes, their mono- and di-cations, and mono- and di-anions are derived. The results obtained are in good agreement with experimental findings for both neutral and charged annulenes.

INTRODUCTION

Annulenes, the monocyclic fully conjugated hydrocarbon family of general formula C_NH_N ($N = 3, 4, 5, \dots$)¹, represent an interesting class of unsaturated cyclic compounds because of their complex chemical and structural properties.² The important development in the chemistry of annulenes started with Hückel's $4m + 2$ rule³, according to which the annulenes with $4m + 2$ π -electrons should exhibit properties different from the annulenes containing $4m$ π -electrons. However, in the Hückel time, the only annulenes known were [6] annulene (benzene), classical aromatic compound, and the non-aromatic [8] annulene (cyclooctatetraene, COT)⁴. Hückel's rule, thus, had a great impact on the development of the annulene chemistry because a number of annulene syntheses are planned in order to prove or disprove this rule⁵. Simultaneously with preparative work, various theoretical indices of aromaticity (*DRE*^{5,6}, *KK*⁷, *REPE*⁸, *A_s*⁹, *RE*¹⁰, etc.) were derived and applied to annulenes in order to predict their aromatic character and to investigate whether Hückel's rule holds for an arbitrary size of the annulene ring or whether there is a critical size at which the $4m + 2$ rule breaks down. Longuet-Higgins and Salem¹¹ predicted the [18] annulene ring system to be of a critical size at which [4m + 2]-annulenes behave like cyclic polyenes with alternating single and double bonds. However, Dewar and Gleicher⁵ used a modification¹² of Pople's SCF π -MO method¹³ parametrized to reproduce the ground state properties. They have found that the critical size at which the bond alternation occurs is between [22]- and [26]-annulene. NMR studies¹⁴ support this result according to which the [4m + 2]-annulenes up to $m = 5$ are aromatic, whereas higher [4m + 2]-annulenes behave as non-aromatic species. Consequently, any theoretical treatment of annulenes must differentiate between [4m + 2] and [4m]-

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classes for m being small and must indicate the convergence between the two classes for m being large.

Recently, we have introduced¹⁵ a new* theoretical index of aromaticity, named topological resonance energy, TRE , which solely depends on the molecular topology and does not require any additional parameter (usually needed by other theoretical methods⁵⁻¹⁰). We therefore thought that annulenes, because of their unique topology (cycles of degree two)¹⁶ and very specific properties, would be a good class of important organic compounds to test the TRE concept. Besides, TRE values can be evaluated for odd-membered annulenes and for annulene ions. Dewar-type theoretical indices, earlier proposed, could not embrace annulene radicals and ions in a simple way. We believe that the possibility of studying all annulene ring systems justifies the present investigation.

THEORETICAL APPROACH

Annulenes are a very simple class of conjugated structures. They exhibit a number of topological regularities. In addition, annulenes possess a high symmetry which allows one to write analytical expressions for their energies and TRE indices.

The starting point in deriving TRE expressions of annulene systems is as follows,

$$TRE = E_{\pi} ([N] \text{ annulene}) - E_{\pi} (\text{reference structure}) \quad (1)$$

where the terms on the right side of eq (1) denote the total HMO π -electron energy (in units β) of $[N]$ annulene and the corresponding reference structure, respectively. In our theoretical approach¹⁵, the reference structure contains all acyclic contributions to E_{π} of a cyclic structure. Thus, TRE represents only cyclic contributions to E_{π} . This definition of resonance energy is the optimal non-empirical realization of Dewar's concept⁵ of resonance energy.

Analytical expressions for E_{π} ($[N]$ annulene) are known^{9,17,18}

$$E_{\pi} ([N] \text{ annulene}) = \begin{cases} 2 (\text{ctg } \Theta - \text{tg } \Theta) & ; N = 4m \\ 2 \text{ctg } \Theta \cos \Theta & ; N = 4m + 1 \text{ or} \\ & N = 4m + 3 \\ 2 (\text{ctg } \Theta + \text{tg } \Theta) & ; N = 4m + 2 \end{cases} \quad (2)$$

where $\Theta = \pi/2N$.

The E_{π} (reference structure) is derived in the following way. The molecular graph representing $[N]$ annulene is a cycle C_N with N vertices (see Figure 1). Let us denote the edge in C_N by e . The excising of the edge e , connecting vertices N and 1 , from C_N leads to chain L_N with N vertices, while removal of e together with incident vertices (e.g. N and $N-1$) produces chain L_{N-2} with $N-2$ vertices (see Figure 1). Let us now consider the possible ways of selecting j non-neighbouring edges in the graph C_N . This may be done in two ways: (i) edge e is not among j edges selected. There are $g_j(L_N)$ selections of this kind. (ii) edge e is among j edges selected. There are $g_{j-1}(L_{N-2})$ selections of this kind. Hence,

$$g_j(C_N) = g_j(L_N) + g_{j-1}(L_{N-2}) \quad (3)$$

* Independently, Aihara (J.-I. Aihara, *J. Amer. Chem. Soc.* **98** (1976) 2750) has developed similar index of aromaticity.

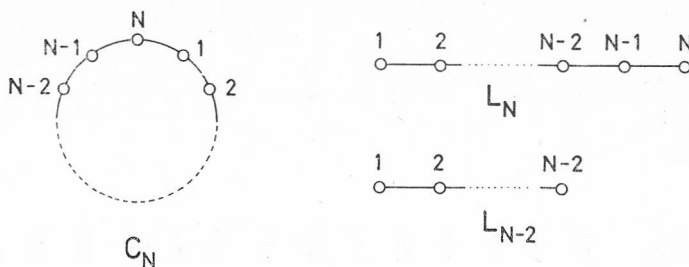


Figure 1.

Note the definition of the polynomial $P(G, x)$,

$$P(G, x) = \sum_j (-1)^j g_j(G) x^{2j} \quad (4)$$

where $g_j(G)$ is a number of possible selections of j mutually non-incident edges in the molecular graph. Thus, it follows from the above considerations

$$\Gamma(C_N, x) = \Gamma(L_N, x) - \Gamma(L_{N-2}, x) \quad (5)$$

The Γ polynomial is defined in such a way that in the acyclic graph it is identical to the characteristic polynomial (P -polynomial) of the same graph¹⁹. Because of this

$$\Gamma(C_N, x) = P(L_N, x) - P(L_{N-2}, x) \quad (6)$$

Since,

$$P(L_N, x) = \frac{\sin(N+1)t}{\sin t} \quad (7)$$

and introducing $x = 2 \cos t$, it follows directly

$$\Gamma(C_N, x) = 2 \cos Nt \quad (8)$$

The roots of the polynomial $\Gamma(C_N, x)$ are given by,

$$\gamma_j = 2 \cos \frac{2j+1}{2N} \pi; \quad j = 0, 1, \dots, N-1 \quad (9)$$

The E_π (reference structure) is related to the roots of the polynomial $\Gamma(G, x)$ ¹⁵,

$$E_\pi (\text{reference structure}) = \sum_j |\gamma_j| \quad (10)$$

Introducing eq (9) in (10), one obtains

$$E_\pi (\text{reference structure}) = 4 \sum_{j=0}^{N-1} \cos \frac{2j+1}{2N} \pi \quad (11)$$

TABLE I
 Topological Resonance Energies per Electron, TRE(PE) and RE Indices of Annulenes

[N] annulene	TRE(PE)	DRE ⁵ (Dewar Gleicher) (eV) ^a	DRE ⁵ (Figeys) kcal/mol ^b	KK ⁷ (Kruszewski, Krygowski) (β)	RE ¹⁰ (Aihara) (β)	REPE ⁸ (Hess, Schaad) (β)	A _s ⁹ (Gutman et al.) (β)	Reference to the preparative work ^c
3	-0.155	-0.534	-24.34	2.000	-1.093	-0.268	-0.472	a
4	-0.307							b
5	-0.060	1.318	10.01	3.528	0.361	0.065	1.012	c
6	0.045							d
7	-0.031	-0.108	-10.78	2.669	-0.529	-0.061	0.139	e
8	-0.073							f
9	-0.019	1.061	6.30	3.426	0.212	0.026	0.891	g
10	0.016							
11	-0.013	0.131	6.58	2.875	-0.351	-0.024	0.335	h
12	-0.032							
13	-0.009	0.689	4.89	3.383	0.151	0.016	0.842	i
14	0.008							
15	-0.007	0.043	4.47	2.975	-0.263	-0.011	0.433	j
16	-0.019							k
17	-0.005	0.382	4.26	3.359	0.117	0.012	0.815	l
18	-0.004	-0.120	3.11	3.035	-0.210	-0.005	0.493	m
19	-0.004							
20	-0.012	0.229	3.86	3.344	0.095	0.010	0.298	n
21	-0.004	-0.305	-2.03	3.075	-0.175	-0.002	0.531	o
22	0.003	-0.054	3.76	3.335	0.081	0.009	0.791	p
23	-0.003							
24	-0.008	-0.339	-1.33	3.105	-0.150	0.000	0.557	
25	-0.003	-0.263	3.57	3.323	0.070	0.008	0.781	r
26	0.002							
27	0.002							
28	-0.006							
29	-0.002							
30	0.002							

where

$$\mu = \begin{cases} \frac{N-2}{2} & ; N = \text{even} \\ \frac{N-1}{2} & ; N = \text{odd} \end{cases} \quad (12)$$

This expression can be further simplified using the technique of Polansky²⁰

$$E_{\pi} \text{ (reference structure)} = \begin{cases} 2 \operatorname{ctg} \Theta / \cos \Theta & ; N = \text{even} \\ 2 \operatorname{ctg} \Theta & ; N = \text{odd} \end{cases} \quad (13)$$

The final *TRE* expressions are obtained by substituting eqs (2) and (13) into (1)

$$TRE \text{ ([N]annulene)} = \begin{cases} 2 \left[\frac{\cos \Theta - 1}{\sin} - \operatorname{tg} \Theta \right] & ; N = 4m \\ 2 \frac{\cos \Theta - 1}{\sin} \cos \Theta & ; N = 4m + 1 \\ & \text{or} \\ & ; N = 4m + 3 \\ 2 \left[\frac{\cos \Theta - 1}{\sin} + \operatorname{tg} \Theta \right] & ; N = 4m + 2 \end{cases} \quad (14)$$

TRE per electron, *TRE* (PE), and RE^{5-10} indices of [N] annulenes are reported in Table I*

Furthermore, the dependence of *TRE* (PE) on the ring size is demonstrated in Figure 2.

Analytical expressions for *TRE* of annulene ions are obtained straightforwardly. Let $(TRE)^0$, $(TRE)^+$, $(TRE)^{++}$, $(TRE)^-$, and $(TRE)^{-}$, respectively denote

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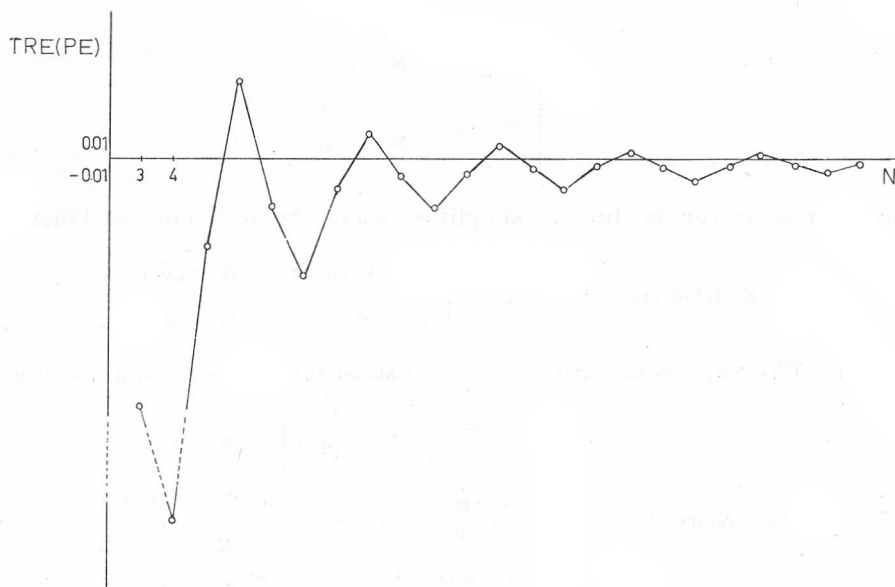


Figure 2.

topological resonance energies of $(C_N H_N)^0$, $(C_N H_N)^+$, $(C_N H_N)^{++}$, $(C_N H_N)^-$, and $(C_N H_N)^{-+}$, respectively.

$$(TRE)^+ = (TRE)^0 - \begin{cases} 2 \sin \Theta & ; N = 4m \\ -2 \sin \Theta & ; N = 4m + 1 \text{ or} \\ 2 \sin \Theta - 2 \sin 2\Theta & ; N = 4m + 3 \\ & ; N = 4m + 2 \end{cases} \quad (15)$$

$$(TRE)^{++} = (TRE)^0 - \begin{cases} 4 \sin \Theta & ; N = 4m \\ 2 \sin \Theta - 4 \sin \Theta & ; N = 4m + 1 \\ 2 (\sin \Theta + \sin 2\Theta - \sin 3\Theta) & ; N = 4m + 3 \\ 4 \sin \Theta - 4 \sin 2\Theta & ; N = 4m + 2 \end{cases} \quad (16)$$

$$(TRE)^- = (TRE)^0 - \begin{cases} 2 \sin \Theta & ; N = 4m \\ -2 \sin \Theta & ; N = 4m + 1 \text{ or} \\ 2 \sin \Theta - 2 \sin 2\Theta & ; N = 4m + 3 \\ & ; N = 4m + 2 \end{cases} \quad (17)$$

$$(TRE)^{-+} = (TRE)^0 - \begin{cases} 4 \sin \Theta & ; N = 4m \\ 2 (\sin \Theta + \sin 2\Theta - \sin 3\Theta) & ; N = 4m + 1 \\ 4 \sin \Theta - 4 \sin 2\Theta & ; N = 4m + 3 \\ 2 \sin 2\Theta - 4 \sin \Theta & ; N = 4m + 2 \end{cases} \quad (18)$$

The results obtained from eqs (15)–(18) for TRE , per electron are given in Table II.

TABLE II
Topological Resonance Energies per Electron (in β) of [N] Annulene Ions

[N] annulene	TRE(PE) ⁺	TRE(PE) ⁺⁺	TRE(PE) ⁻	TRE(PE) ⁻⁻	Reference to the preparation work		
					cation	dication	dianion
3	0.268	0.268	-0.366	-0.146	a		
4	-0.154	0.152	-0.092	0.051			
5	-0.306	-0.121	-0.053	-0.018			b
6	-0.042	-0.173	-0.030	-0.087			
7	-0.031	-0.031	-0.083	-0.027	b		
8	-0.029	0.031	-0.023	0.018		g	h, i
9	-0.065	-0.026	-0.018	-0.013			i
10	-0.016	-0.056	-0.013	-0.038	c, d		
11	0.014	-0.014	-0.036	-0.011			
12	-0.012	0.013	-0.010	0.009			m
13	-0.030	-0.011	0.009	0.007			
14	-0.008	-0.027	0.007	-0.021			j
15	0.008	-0.007	-0.020	-0.006	e, f		k
16	-0.007	0.007	-0.006	0.005			
17	-0.017	-0.006	0.005	-0.005			l
18	-0.005	-0.016	-0.004	-0.013			
19	0.005	-0.005	-0.012	-0.004			
20	-0.004	0.004	-0.004	0.003			
21	-0.011	-0.004	0.003	-0.003			
22	-0.003	-0.011	-0.003	-0.009			
23	0.003	-0.003	-0.008	-0.003			
24	-0.003	0.003	-0.003	0.002			n

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In addition, the dependence of $TRE(PE)^+$, $TRE(PE)^{++}$, $TRE(PE)^-$, and $TRE(PE)^{-}$ on the annulene ring size is represented in Figure 3.

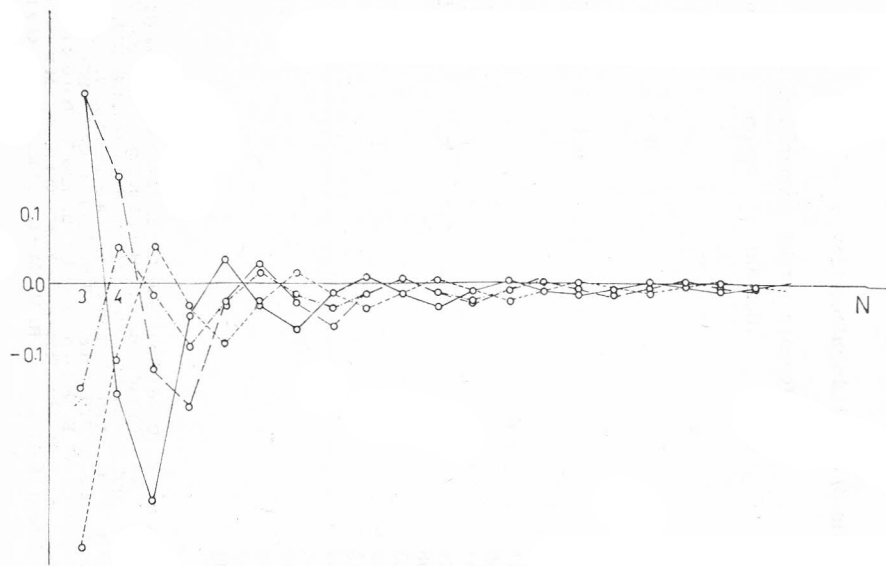


Figure 3.

DISCUSSION

Analysis of eq (14) and Figure 2 shows that $[4m + 2]$ - and $[4m]$ -annulenes become rapidly non-aromatic compounds with increasing value of m and that the differences between them practically disappear. Thus, [18]-annulene is predicted to be a cyclic polyene ($TRE(PE) = 0.005\beta$) (a compound is considered non-aromatic if its $TRE(PE) < 0.010\beta$ and $> -0.010\beta$). Some other theoretical predictions (*REPE* index⁸) opposes to our result, but a recent, very thorough MINDO/3 study²¹ of [18] annulene (its geometry was calculated by minimizing the energy with respect to all 102 internal coordinates) indicates negligible π -electron delocalization. Experimental evidence shows that [18] annulene fails to undergo electrophilic substitution reactions²² unless the reaction is carried out under very specific conditions²³.

The TRE index neglects steric effects. Thus, all annulenes are assumed to be planar. This assumption is not realistic in those annulenes in which the repulsion between the annulene inner hydrogen atoms considerably affects the total molecular energy. For example, [10] annulene ($TRE(PE) = 0.016\beta$) may appear in two forms (I and II) which are both non-planar²⁴.

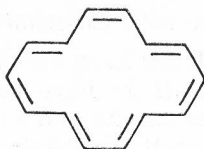


I



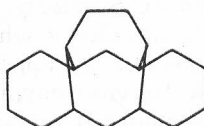
II

The repulsion between the inner hydrogen atoms in [14] annulene ($TRE(PE) = 0.008 \beta$) is smaller than in [10] annulene. [14] annulene is the most stable in the planar form III².



III

Bridged [14] annulenes have also been synthesized²⁵ and the NMR spectrum of IV, for example, indicates that this compound is diatropic.



IV

This structure is aromatic, because there is no interference from the inner hydrogen atoms which are removed by the bridge. [22]-, [26]-, and [30]-annulene have been prepared^{2,26,27}. They differ in their stabilities, [22] annulene ($TRE(PE) = 0.003 \beta$) being the most stable and [30] annulene ($TRE(PE) = 0.002 \beta$) the least stable of these three compounds, however all of them exhibit cyclopolyene characteristics.

A considerable amount of preparative work has also been carried out on [4 *m*] annulenes. Attempts to make [4] annulene (cyclobutadiene, $TRE(PE) = -0.307 \beta$) are classical examples in this respect²⁸. [8] annulene ($TRE(PE) = 0.075 \beta$) is not a planar compound²; its planar form would be a highly unstable anti-aromatic species. [12] annulene ($TRE(PE) = -0.032 \beta$) was synthesized at very low temperature²⁹. [16] annulene was also prepared³⁰ at 273 K and was observed to be a reasonable stable compound. Similarly, [20] annulene ($TRE(PE) = -0.012 \beta$) and [24] annulene ($TRE(PE) = -0.008 \beta$) are known to exhibit non-aromatic properties^{2,26}. Thus, experimental data for both [4 *m*] and [4 *m* + 2] annulenes with large *m* (*m* > 4) exhibit polyolefinic character and support predictions of the *TRE* index.

TRE values of odd annulenes, [4 *m* + 1] and [4 *m* + 3] annulenes (see Figure 3) indicate that the stability of these systems does not depend on the ring size. Some of these compounds, e. g. (C_7H_7), (C_5H_5) are observed as short-lived species^{31,32}.

Considerable progress in the chemistry of charged annulenes has been achieved in the last decade with the introduction of novel preparative techniques³³. Thus, (C_3H_3)⁺, (C_3H_3)⁻, (C_7H_7)⁺, (C_8H_8)⁺⁺, (C_8H_8)⁻⁻, and (C_9H_9)⁻ were predicted to be aromatic ions and are all prepared in solution³⁴⁻⁴¹. All these compounds, follow 4 *m* + 2 π -electron Hückel's rule^{3,42}. It is interesting to note that in the case of cyclooctatetraene (COT) the parent compound and all ions

were prepared except COT^+ . The TRE (PE) index gives the following ordering of COT and its ions

$$\text{COT}^{++} \approx \text{COT}^{--} > \text{COT}^+ \approx \text{COT}^- > \text{COT}^0$$

This result is in full agreement with experimental findings.

Some higher charged annulenes have also been prepared. Thus, $(\text{C}_{11}\text{H}_{11})^+$, $(\text{C}_{13}\text{H}_{13})^-$, $(\text{C}_{15}\text{H}_{15})^+$, $(\text{C}_{16}\text{H}_{16})^-$, $(\text{C}_{24}\text{H}_{24})^-$ have been prepared recently, though some of them with various substituents and some with bridges⁴³⁻⁴⁸. An interesting prediction has been reached for dianions of $[4m]$ -systems. These are predicted to be much more stable (for $m < 5$) than the parent compound. Thus, $(\text{C}_4\text{H}_4)^{--}$ was observed⁴⁹ to be relatively stable. Similarly, $(\text{C}_{10}\text{H}_{10})^{--}$ remained unchanged after boiling in tetrahydrofuran- d_8 at 373 K⁴⁷. Therefore, $[4m]$ annulenes could be converted into aromatic dianionic $4m + 2$ π -electron systems. Our TRE (PE) index closely follows these considerable changes in stabilization. (Compare Figures 2 and 3). Similarly, the opposite effect should be expected in the case of $[4m + 2]$ annulenes when converted to dianionic $4m$ π -electron systems. A remarkable change appears in the NMR spectrum of $(\text{C}_{18}\text{H}_{18})^-$ when compared with the parent compound. $(\text{C}_{18}\text{H}_{18})$ is very paratropic, in accord with a 20 π -electron system⁵⁰ it represents.

In all cases studied the TRE (PE) index closely follows experimental findings and thus it proves the predictive power of the topological method used here. However, Dewar's resonance energies, DRE are very useful in the case of neutral even annulenes (TRE index has the advantage over DRE in the case of odd and charged annulenes). It would, therefore be interesting to investigate the relationship between TRE and DRE indices. The E_π (reference structure) of annulene is given by,

$$E_\pi \text{ (reference structure)} = A n_+ + B n_- \quad (19)$$

where A and B are constants. The values of A and B are 2.00β and 0.52β , respectively in the approach of Milun et al.⁵¹ and 2.0699β and 0.4660β , respectively in the Hess and Schaad model⁸. Since n_+ and $n_- = N/2$ for $[N]$ annulenes, it follows that both approaches give a similar expression for the π -electron energy of the reference structure

$$E_\pi \text{ (reference structure)} = 1.27 N \quad (20)$$

E_π (reference structure) in TRE theory is not a linear function of N . However, the following approximations can be used: $\sin \Theta \approx 0$ and $\cos \Theta \approx 1$ (these approximations are quite reasonable for large N) in eq (13). Then, it follows

$$E_\pi \text{ (reference structure)} \approx \frac{4}{\pi} N = 1.27 N \quad (21)$$

Therefore, eqs (20) and (21) are equal. In the DRE approach of Hess and Schaad this equality is conditioned by the particular selection of bond parameters. This also indicates that topology is the backbone of DRE approach, at least for annulenes.

CONCLUSIONS

As it has already been pointed out, the TRE method has several important advantages over the DRE method. These are:

(a) *TRE* is an optimal non-parametric realization of Dewar's concept of resonance energy; (b) *TRE* contains all cyclic and no acyclic contributions to π -electron energy of a molecule; (c) *TRE* is applicable to an arbitrary conjugated system, and (d) *TRE* allows a derivation of simple analytical formulae for *TRE* of both neutral and charged annulenes.

The available experimental data support *TRE* predictions, so that the *TRE* method can be considered as a powerful tool for estimating the aromatic stability of annulenes and related compounds.

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SAŽETAK

Topološke rezonancijske energije anulena

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Nedavno razvijena koncepcija topološke rezonancijske energije, *TRE* (optimalne neparametarske realizacije Dewarove rezonancijske energije), primijenjena je na *TRE* neutralnih anulena i njihovih mono- i di-kationa i aniona. Dobiveni rezultati dobro se slažu s eksperimentalno nadenim činjenicama, kako za neutralne anulene, tako i za njihove ione.

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