Aromaticity study on tria-, penta- and hepta-fulvene derivatives

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ARTICLE INFO

ABSTRACT

Aromaticity of 70 mono-exocyclically tria-, penta- and hepta-fulvene derivatives, included H, CH₃, CCH, CMe₃, CN, CONH₂, COCH₃, CF₃, CH₂⁻, CC⁻, COO⁻, F, B(OH)₂, OH, OCH₃, O⁻, NH₂, NO₂, NO, NMe₂, NH⁻, NH₃⁺, NN⁺, SiMe₃ substituents, are investigated using recently introduced Shannon Aromaticity (SA) index and some other geometric (HOMA), magnetic (different NICSs) and energetic (ISE) indices. Wide range of variation in these indices indicates to the considerable sensitivity of π-electron structure of a fulvene ring to the substituent. It is shown that although the obtained SA and HOMA values predict the aromatic character of the considered molecules, NICS-related indices predict a relatively high aromaticity/anti-aromaticity for all tria-/hepta-fulvenes. The best correlation is observed between the SA and HOMA indices and it is also shown that the former shows a significant correlation with the GEO part of HOMA index, which is due to bond alternation, rather than EN contribution, which is arisen from bond elongation.

1. Introduction

Aromaticity is a theoretical concept of great practical importance [1]. It is one of the most widely used concepts in chemistry, biochemistry and biology. Since this concept is not a directly observable quantity, it is usually evaluated indirectly by measuring a property that reflects the aromatic character of the whole or parts of the molecule. Based on the molecular property from which the aromaticity index is derived, all existent criteria can be divided into a few basic categories such as geometrical [2], magnetic [3–6], electronic [7] and energetic [8]. It should be mentioned that because of the multidimensionality of aromaticity, all indices do not always give consistent results among themselves; and sometimes different aromaticity values derived from different indices lead to different aromaticity order [9].

Variation in geometry is a very important source of information about aromaticity [10]. The Harmonic Oscillator Model of Aromaticity (HOMA) is one of the most widely used geometrical-based indices, which is defined as [11]:

$$HOMA = 1 - \left[\alpha(R_{opt} - R_{av})^2 + \frac{\alpha}{n}\sum(R_{av} - R_i)^2 \right] = 1 - EN - GEO \tag{1}$$

where n is the number of considered bonds in the summation, R_{av} is the average bond length and α is a normalization constant (for C—C bonds $\alpha = 257.7$), fixed to give HOMA = 0 for a model of non-aro-

matic system and HOMA = 1 for the system with all bonds equal to the optimum value assumed to be achieved for fully aromatic system (for C—C bond $R_{opt} = 1.388$ Å). EN and GEO parts of the HOMA index describe a decrease in aromaticity due to bond elongation and bond alternation, respectively.

Magnetic criteria are based on this fact that π-electron ring current is induced when the system is exposed to an external magnetic field. Undoubtedly, the most widely used magnetic–based index, which is proposed by Schleyer and coworkers [12], is the Nucleus-Independent Chemical Shift (NICS). This index is defined as the negative value of the absolute shielding which is computed at the center (NICS(0)) or at some other points of a cyclic system (NICS(r)). For instance, NICS(1) is defined as the computed negative value of the absolute magnetic shielding at 1 Å over the ring plane. Rings with negative and positive NICS values are considered as aromatic and anti-aromatic, respectively. The total contribution of the out-of-plane component of the NICS tensor (NICS$_{zz}$), is another NICS-based index of aromaticity. It should be mentioned that the NICS-based indices are depended on the area of the ring. Although many theoreticians have used the NICS to explain the aromatic/anti-aromatic behavior of various compounds [13–17], in some cases it is not a reliable indicator and leads to an incorrect prediction of aromaticity [18,19].

Indices of aromaticity based on energetic properties, make use of the fact that conjugated cyclic π-electron compounds are more stable than their chain analogs. The isomerization method [20,21] is based on the difference between total energies computed for a methyl derivative of the aromatic system and its structurally closely related non-aromatic exocyclic methylene isomer. This difference is called Isomerization Stabilization Energy (ISE = E(CH₂)-

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E(CH$_3$)) and is a measure of aromatic stabilization. Systems with positive and negative ISE values are considered as aromatic and anti-aromatic, respectively. This method is easily and successfully used for prediction of aromaticity in different systems [22–26].

It is well-known that the electronic structure of a molecule is strongly connected to its aromaticity. For instance, recently AIM parameters at the ring critical points (RCP) of some six-membered aromatic and quasi-aromatic molecules are used for estimation of π-electron delocalization [27].

Recently [28], using the definition of Shannon Entropy [29] and the obtained electron densities at the bond critical points (BCPs) of a molecule ($\rho(r_c)$), a new electronic-based aromaticity descriptor is introduced, which is called Shannon Aromaticity (SA):

$$SA = \ln(N) - \sum_{i=1}^{N} (p_i)\ln(p_i) = S_{max}(r_c) - S_{total}(r_c) \qquad (2)$$

in which N is the number of considered BCPs in the ring and p_i, which is defined as $p_i = \frac{\rho_i(r_c)}{\sum_i \rho_i(r_c)}$, is the normalized probability electron density at the ith BCP. It is shown that the calculated SA index for a given molecule can be used as a measure of the spatial localization of the electron density and therefore less SA values are corresponded to those molecules which are more aromatic. The range of $0.003 < SA < 0.005$ is also considered as the boundary between aromatic and anti-aromatic compounds; i.e. non-aromatic systems. This index is successfully applied to explain the global aromaticity behaviors of some five-membered heterocycles, mono-substituted benzene rings, and also local aromaticities of nonbenzeneoid, linear and angular polyacenes systems [28].

Fulvenes, conjugated rings with one exocyclically C=C double bond, are among the most attractive classical non-alternant π-electron systems. The substituted fulvenes represent an interesting group of systems for a systematic study of the extent of changes in the cyclic π-electron delocalization due to substitution. Aromaticities of the fulvene rings vary to some extent depending on the electronic character of the substituent. According to the unique cross conjugated structure, which can generate both $(4n + 2)$ and $(4n)$ π-electron species via bond polarization (see Scheme 1), fulvenes and their derivatives have been the subject of various studies [30–41] and some attempts have been made to investigate the aromaticity characters of these systems [42–44]. Very recently Fowler et. al. investigated aromatization of fulvene by complexation with lithium atom [45].

The main purpose of this study is checking the ability of Shannon Aromaticity descriptor in predicting the aromatic character of mono-exocyclically substituted tria-, penta- and hepta-fulvene derivatives. The relationships between this new index and some other commonly used aromaticity indices, such as HOMA, ISE and different NICSs, are investigated and a comparison is also made between the considered indices.

2. Computational details

A set of various mono-exocyclically tria-, penta- and hepta-fulvenes are selected, which included H, CH$_3$, CCH, CMe$_3$, CN, CONH$_2$, COCH$_3$, CF$_3$, CH$_2^-$, CC$^-$, COO$^-$, F, B(OH)$_2$, OH, OCH$_3$, O$^-$, NH$_2$, NO$_2$, NO, NMe$_2$, NH$^-$, NH$_3^+$, NN$^+$, SiMe$_3$ substituents (see Scheme 2). These substituents are just arranged according to their attaching atoms of R group (H, C, N, O, F, B and Si atoms). Geometries of all considered compounds are fully optimized at B3LYP/6-31 + G** level of theory and their minimum nature are checked by frequency analysis at the same computational level. Chemical shieldings are calculated under the GIAO approximation [46] and HF/6-31 + G** method at the corresponding ring critical points. It should be mentioned that, DFT methods do not provide systematically better shielding results than the HF methods [47]. In order to calculate the ISE values, all the methyl and methylene isomers of the considered molecular systems are optimized at B3LYP/6-31 + G** level of theory. Vibrational frequencies are also calculated to obtain corrected zero-point energies and to verify that the optimized structures are minima on the potential energy surfaces. Since it was demonstrated that the position of the methyl group is seldom critical [22], therefore only one choice for the placement of the methyl and methylene groups has been considered, which are shown with star in Scheme 2. All calculations are performed with the help of Gaussian 98 W suite of program [47]. Electron densities at BCPs and AIM parameters at RCP of the optimized structures are calculated using the electronic wave functions and AIM2000 software [48].

3. Results and discussion

Following the Huckel $(4n + 2)$ rule, an electron accepting substituent causes an increase in the aromatic character of tria- and hepta-fulvene rings (**1b** and **3b** in Scheme 1), which is due to decrease of the weight of 4π- and 8π-electron resonance structures. On the other hand, these substituents decrease the weight of 6π-electron resonance form of penta-fulvene rings (**2a** in Scheme 1), and therefore they decrease the aromaticity of these systems.

The obtained HOMA values for the considered tria-, penta- and hepta-fulvenes, together with the EN and GEO contributions, are gathered in Tables 1–3, respectively. These values are based on the optimized molecular geometries at B3LYP/6-31 + G** level of theory. Different NICSs (NICS(0), NICS(1) and NICS$_{zz}$(1)) and the obtained SA values from Eq. (2) are also summarized in these tables. The most and the least values in each column are bolded. The obtained electron densities at BCPs of each ring and the corrected energies of the methyl and methylene forms of these derivatives, are summarized in Tables S1–S4 of Supplementary materials. Note
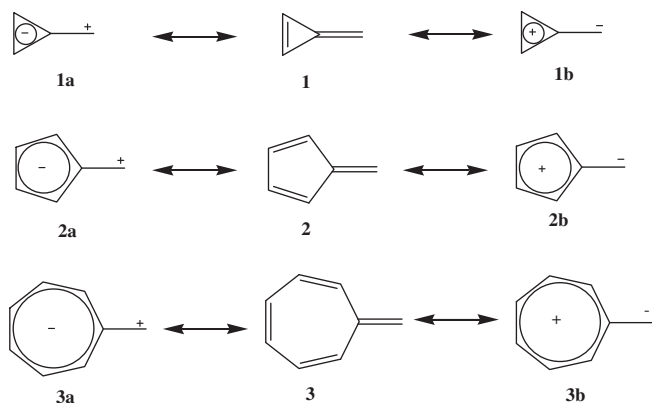
Scheme 1. Canonical structures of tria-, penta- and hepta-fulvenes.
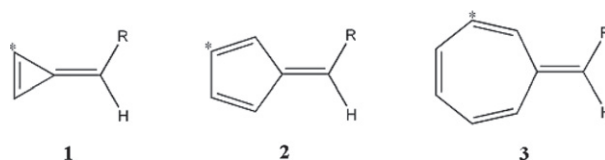
R= a) H, b) CH$_3$, c) CCH, d) CMe$_3$, e) CN, f) CONH$_2$, g) COCH$_3$, h) CF$_3$, i) CH$_2^-$, j) CC$^-$, k) COO$^-$, l) F, m) B(OH)$_2$, n) OH, o) OCH$_3$, p) O$^-$, q) NH$_2$, r) NO$_2$, s) NO, t) NMe$_2$, u) NH$^-$, v) NH$_3^+$, w) NN$^+$, x) SiMe$_3$

Scheme 2. Structures of the studied compounds.

Table 1
Calculated EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$, ISE and SA for mono-substituted tria-fulvene derivatives.

Molecule	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE[a]	SA $\times 10^2$
1a	0.064	0.846	0.091	−23.43	−8.10	−13.65	−4.171	0.669
1b	0.084	0.922	−0.006	−23.31	−7.54	−12.29	−6.621	0.751
1c	0.028	0.687	0.284	−24.66	−9.30	−15.43	−2.325	0.543
1d	0.084	0.944	−0.027	−22.91	−7.31	−11.22	−6.038	0.765
1e	0.014	0.606	0.381	−25.62	−10.24	−17.35	1.638	0.476
1f	0.034	0.735	0.231	−24.90	−10.21	−17.25	1.610	0.588
1g	0.024	0.672	0.304	−24.69	−9.58	−16.36	2.456	0.526
1h	0.019	0.676	0.306	−25.56	−9.99	−16.86	−0.050	0.533
1j	0.142	1.022	−0.172	−20.51	−5.09	−7.28	−24.46	0.835
1k	0.010	0.909	−0.009	−21.59	−7.17	−11.63	−13.767	0.702
1l	0.064	0.969	−0.036	−25.67	−7.53	−13.39	−7.844	0.828
1m	0.030	0.667	0.303	−23.42	−9.44	−15.51	−0.658	0.501
1n	0.073	0.954	−0.027	−24.55	−6.99	−11.87	−10.250	0.799
1o	0.072	0.946	−0.021	−24.48	−8.24	−13.45	−9.855	0.795
1p	0.548	1.832	**−1.379**	**−14.74**	**2.07**	**2.92**	**−44.955**	**1.694**
1q	0.117	1.071	−0.187	−23.65	−5.99	−9.61	−13.554	0.918
1r	0.002	0.523	0.475	−26.63	−10.93	−19.44	4.085	0.407
1s	0.002	0.496	0.502	−24.07	−9.41	−18.30	5.486	0.379
1t	0.113	1.086	−0.198	−22.50	−7.91	−11.83	−13.559	0.920
1v	0.010	0.680	0.310	−28.26	−10.80	−18.99	5.767	0.601
1w	0.016	0.224	**0.770**	**−28.90**	**−13.50**	**−23.79**	**18.703**	**0.208**
1x	0.064	0.814	0.122	−22.69	−8.52	−13.23	−2.446	0.639

[a] ISE values are in kcal mol^{-1}.

Table 2
Correlation coefficients between SA, EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$ and ISE indices for mono-substituted tria-fulvene derivatives.

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$
EN	0.843						
GEO	0.985	0.793					
HOMA	0.988	0.884	0.984				
NICS(0)	0.676	0.743	0.727	0.764			
NICS(1)	0.902	0.851	0.915	0.939	0.844		
NICS(1)$_{zz}$	0.900	0.797	0.934	0.938	0.857	0.972	
ISE	0.888	0.779	0.918	0.921	0.816	0.938	0.959

Table 3
Correlation coefficients between the used aromaticity indices and the parameters of electron density function at RCP for the considered tria-fulvene derivatives.

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE
ρ	0.926	0.741	0.971	0.948	0.804	0.919	0.968	0.946
G	0.947	0.725	0.985	0.953	0.747	0.912	0.948	0.941
V	0.932	0.715	0.978	0.944	0.766	0.908	0.954	0.940
H	0.902	0.697	0.958	0.923	0.790	0.895	0.956	0.932

that the maximum Shannon entropies (S_{max}) of tria-, penta- and hepta-fulvenes for the calculation of SA are ln(3), ln(5) and ln(7), respectively.

The calculated indices for tri-fulvene rings are collected in Table 1. It should be mentioned that when a three-membered ring is substituted with CH_2^- or NH^- group, the ring is opened during the geometry optimization; therefore these two derivatives (**1i** and **1j**) are excluded from this table. A wide range of variation in the reported values indicates to the considerable effect of substituent on the aromatic character of these systems. Although the obtained SA, ISE and HOMA values illustrate this point very well ($0.208 < SA \times 10^2 < 1.694$, $-44.955 < ISE < 18.703$ and $-1.379 < HOMA < 0.761$), NICS values just predict a relatively small variation in the aromaticities of the rings with the change of substituent (for instance $-14.74 < NICS(0) < -28.90$). On the other hand, ISE, HOMA and SA values predict high anti-aromatic and aromatic characters for the electron donating (such as O^- with HOMA = −1.379, ISE = −44.955 and SA $\times 10^2$ = 1.694) and electron accepting groups

(such as NN^+ with HOMA = 0.7601 ISE = 18.703 and SA $\times 10^2$ = 0.208), respectively. This follows the Huckel rule. But all NICS-based values incorrectly predict high aromaticity for all of these tria-fulvene derivatives. It seems that tria-fulvenes are special case. Due to the local effect of the nearby double bond in these small rings, the NICS values are strongly diatropic.

The HOMA index in the form of its contributions (EN and GEO terms) is better to understand the consequences of the substituent effect on the π-electron delocalization structure of a ring. According to the results of Table 1, it is obvious that in all cases the values of the GEO term are more than the EN term values. Therefore it seems that the bond alternation is more contributed in the aromatic character of these systems than the bond elongation. The results in this table also indicate that the GEO term decreases/ increases considerably from 0.846 for the unsubstituted tria-fulvene (**1a**) to 0.224/1.832 for the NN^+ (**1w**)/O^- (**1p**); while the changes in the EN term of different molecules are not considerable (from 0.064 for **2a** to 0.010/0.548 for **1v**/**1p**). Hence it seems that the bond alternation is mostly affected by the intermolecular charge transfer between the electron donating or electron accepting substituent and the ring. Surprisingly, the calculated SA values are better correlated with the GEO contribution of HOMA (R^2 = 0.985) rather than the EN part (R^2 = 0.843) (see Figs. S1 and S2 in Supplementary materials). It may arise from this fact that both SA and GEO concepts have something to do with the similarity of electron distributions in different bonds of a given molecule.

As it is shown in Table 2, the correlation coefficients between the values of HOMA and SA with different NICSs are not satisfactory; whereas the obtained HOMA and SA values for the considered tria-fulvene derivatives are significantly correlated to each other with R^2 = 0.988 (see Fig. 1).

The calculated parameters of the electron density function at RCP (included electron density, ρ, total electron energy density, H, kinetics electron energy density, G, and potential electron energy density, V) for the considered tria-fulvene derivatives are collected in Table S5 of Supplementary materials. The obtained correlation coefficients between these parameters and the other aromaticity indices are given in Table 3. It is clear that each of the mentioned parameters show a good correlation with the other indices.
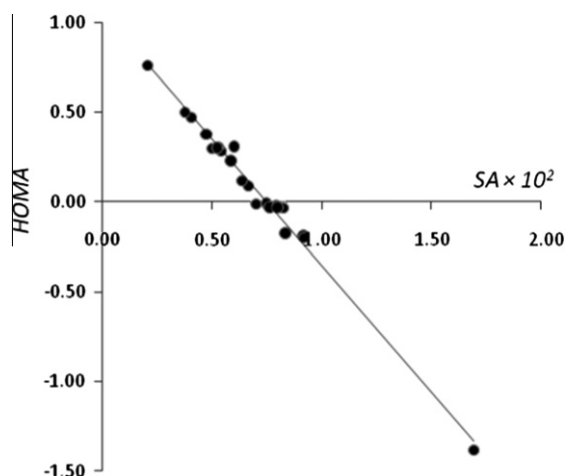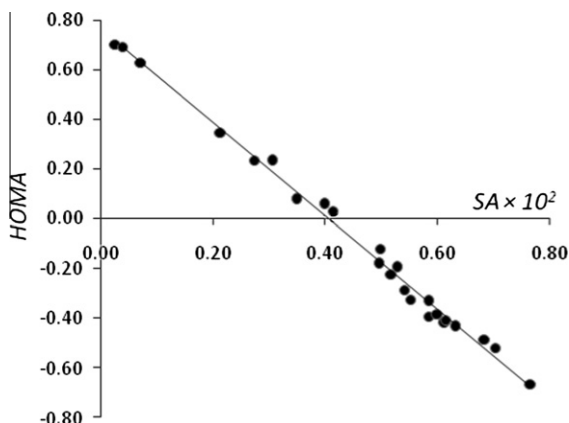
Fig. 1. The correlation between the calculated HOMA and SA values for tria-fulvene derivatives.

Table 5
Correlation coefficients between SA, EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$ and ISE for mono-substituted penta-fulvene derivatives.

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$
EN	0.951						
GEO	0.996	0.952					
HOMA	0.993	0.966	0.996				
NICS(0)	0.934	0.895	0.933	0.931			
NICS(1)	0.897	0.847	0.890	0.887	0.985		
NICS(1)$_{zz}$	0.926	0.872	0.920	0.916	0.996	0.988	
ISE	0.939	0.881	0.941	0.937	0.940	0.888	0.932

of the ring is more affected by a considerable increase in bond alternation (GEO) rather than a negligible increase in bond elongation (EN). Again the calculated SA values are well correlated with the GEO contribution of HOMA ($R^2 = 0.996$) rather than the EN part ($R^2 = 0.952$) of this index (see Figs. S3 and S4 in Supplementary materials).

The results show that good correlations are observed not only between those indices which have the same background, but also for those which are based on different properties; for instance HOMA vs NICS(0) with $R^2 = 0.931$; or SA vs NICS(0) with $R^2 = 0.934$. This point is well illustrated by the represented correlation coefficients in Table 5. Note that again the best correlation is observed between the obtained SA values and HOMA index with $R^2 = 0.993$ (see Fig. 2).

The correlations between the obtained electron density function parameters at RCP (ρ, H, G and V) and the other aromaticity indices are also investigated for the considered penta-fulvene derivatives. The calculated parameters, which are gathered in Table S6 of Supplementary materials, do not show a good correlation with the other indices (see Table 6).

The obtained results for the considered hepta-fulvene derivatives are summarized in Table 7. The sensitivity of these molecular systems to the substitution effect is obvious. As in the case of tria-fulvene rings, for electron accepting substituents (such as NN$^+$ with HOMA = 0.808, ISE = 20.474 and SA $\times 10^2$ = 0.062), the hepta-fulvene derivatives show high aromaticity; whereas electron donating groups (such as CH$_2^-$ with HOMA = 0.030 and SA $\times$

The evaluated results for the selected penta-fulvene systems are gathered in Table 4. As in the case of tria-fulvenes, the aromaticities of the penta-fulvene rings are extremely sensitive to the substituents. But in contrast with the tria-fulvene rings, for electron donating substituents (such as CH$_2^-$ with HOMA = 0.704 and SA $\times 10^2$ = 0.027), the five-membered ring of the system shows high aromaticity; whereas electron accepting substituents (such as NN$^+$ with HOMA = −0.668 and SA $\times 10^2$ = 0.767) decrease the number of 6π-electron of the ring and hence increase the anti-aromatic character of the system. According to this table, although all indices predict **2w** (R=NN$^+$) as the most anti-aromatic compound among the considered derivatives, in the case of electron donating groups no regularity is observed between the aromaticity indices. Different NICSs and ISE values predict **2u** (R=NH$^-$) as the most aromatic system, while HOMA and SA indices predict it is **1i** (R=CH$_2^-$). It is also clear from this table that GEO/ EN varies from 0.876/0.411 for unsubstituted **2a** to 1.985/0.470 for **2w**. Therefore it seems that for an electron accepting substituent, the decrease in aromaticity

Table 4
Calculated EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$, ISE and SA for mono-substituted penta-fulvene derivatives.

Molecule	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE[a]	SA $\times 10^2$
2a	0.411	0.876	−0.287	−0.65	−3.52	−6.64	1.664	0.542
2b	0.390	0.791	−0.182	−1.78	−4.16	−8.50	2.586	0.496
2c	0.382	0.814	−0.196	0.52	−2.62	−3.14	1.311	0.528
2d	0.403	0.820	−0.223	−1.72	−3.98	−7.52	3.260	0.519
2e	0.407	0.927	−0.333	2.37	−1.49	0.70	−0.877	0.584
2f	0.441	0.981	−0.421	2.90	−1.05	1.73	−0.778	0.614
2g	0.433	0.950	−0.383	1.22	−2.08	−1.71	−1.632	0.600
2h	0.439	0.997	−0.435	1.35	−2.08	−1.34	−0.057	0.632
2i	0.251	0.045	**0.704**	−12.31	−9.63	−29.67	20.683	**0.027**
2j	0.302	0.351	0.347	−7.05	−7.11	−18.87	10.353	0.215
2k	0.357	0.566	0.077	−4.38	−6.80	−14.00	3.770	0.350
2l	0.365	0.757	−0.123	−2.51	−4.15	−8.17	3.534	0.498
2m	0.442	0.952	−0.394	1.51	−2.14	−2.15	0.059	0.585
2n	0.336	0.636	0.029	−3.74	−4.97	−11.24	5.405	0.415
2o	0.331	0.612	−0.057	−3.96	−5.12	−11.66	4.439	0.399
2p	0.254	0.116	0.631	−11.88	−9.69	−29.21	17.415	0.072
2q	0.297	0.470	0.233	−6.01	−6.36	−16.09	6.959	0.307
2r	0.448	1.038	−0.487	4.04	−0.04	5.00	−2.494	0.687
2s	0.429	0.981	−0.410	3.43	−0.09	1.45	−2.410	0.614
2t	0.308	0.455	0.237	−7.51	−7.71	−20.19	9.704	0.274
2u	0.244	0.062	0.693	**−12.71**	**−9.98**	**−30.32**	**23.210**	0.039
2v	0.449	1.071	−0.521	3.42	−0.68	3.63	−2.856	0.703
2w	0.470	1.199	**−0.668**	12.12	5.26	22.38	**−11.092**	**0.767**
2x	0.428	0.897	−0.325	0.04	−3.11	−5.02	−1.410	0.553

[a] ISE values are in kcal mol^{-1}.

Fig. 2. The correlation between the calculated HOMA and SA values for penta-fulvene derivatives.
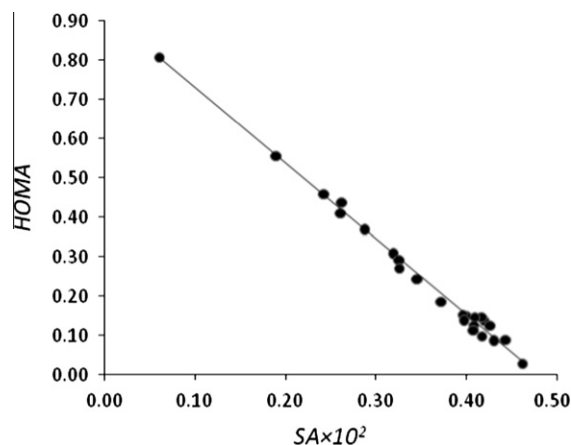

Fig. 3. The correlation between the calculated HOMA and SA values for hepta-fulvene derivatives.

$10^2 = 0.462$) decrease the aromatic character of these systems; which are in accordance with the Huckel $(4n + 2)$ rule. It is also clear from this table that although different NICSs and ISE values predict anti-aromatic character for the molecules which are substituted with electron donating groups (for instance CH_2^- with NICS(0)= 72.59 and ISE = −8.185), the obtained HOMA and SA values predict relatively non-aromaticity for theses derivatives (for example HOMA = 0.140 and SA × 10^2 = 0.397 for CH_2^-). All indices

Table 6

Correlation coefficients between the used aromaticity indices and the parameters of electron density function at RCP for the considered penta-fulvene derivatives.

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE
ρ	0.691	0.800	0.705	0.713	0.584	0.538	0.561	0.558
G	0.140	0.211	0.144	0.150	0.088	0.077	0.084	0.083
V	0.159	0.232	0.164	0.169	0.099	0.085	0.094	0.096
H	0.233	0.263	0.236	0.237	0.129	0.098	0.121	0.162

Table 7

Calculated EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$, ISE and SA for mono-substituted hepta-fulvene derivatives.

Molecule	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE[a]	SA × 10^2
3a	0.185	0.661	0.154	8.40	4.18	14.86	6.428	0.395
3b	0.189	0.661	0.150	8.86	4.57	16.18	5.231	0.399
3c	0.153	0.537	0.310	6.73	2.60	10.69	7.988	0.319
3d	0.196	0.678	0.123	9.27	4.26	18.55	4.256	0.408
3e	0.140	0.490	0.371	4.62	0.70	5.12	9.229	0.288
3f	0.173	0.582	0.245	4.81	0.17	4.66	8.694	0.345
3g	0.143	0.447	0.411	3.17	−0.44	−1.38	10.176	0.261
3h	0.157	0.549	0.294	4.87	1.03	6.11	7.782	0.326
3i	0.230	0.629	0.140	31.97	23.41	72.59	**−8.185**	0.397
3j	0.260	0.710	**0.030**	30.32	22.58	70.25	0.879	**0.461**
3k	0.212	0.674	0.114	10.25	5.36	14.65	4.019	0.407
3l	0.180	0.672	0.148	8.58	4.51	16.16	5.280	0.416
3m	0.170	0.557	0.273	6.09	2.02	8.65	7.855	0.326
3n	0.187	0.688	0.125	10.46	6.11	20.73	4.656	0.425
3o	0.185	0.678	0.138	10.71	6.33	21.48	4.414	0.419
3p	0.230	0.681	0.089	32.57	25.01	75.40	−4.103	0.430
3q	0.198	0.710	0.090	9.97	4.87	18.33	3.173	0.442
3r	0.131	0.410	0.460	1.84	−1.70	−2.12	10.726	0.243
3s	0.118	0.324	0.557	0.96	−2.53	−4.41	12.297	0.190
3t	0.187	0.666	0.147	8.61	3.23	14.41	4.634	0.409
3u	0.237	0.664	0.010	**37.43**	**29.00**	**87.05**	−5.923	0.417
3v	0.129	0.434	0.438	2.15	−1.39	−0.97	12.171	0.262
3w	0.067	0.125	**0.808**	**−0.82**	**−4.20**	**−8.68**	**20.474**	**0.062**
3x	0.185	0.628	0.187	7.49	3.35	12.75	7.190	0.372

[a] ISE values are in kcal mol^{-1}.

Table 8

Correlation coefficients between SA, EN, GEO, HOMA, NICS(0), NICS(1), NICS(1)$_{zz}$ and ISE for mono-substituted hepta-fulvene derivatives.[a]

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$
EN	0.836						
GEO	0.991	0.712					
HOMA	0.993	0.889	0.971				
NICS(0)	0.362 (0.905)	0.690 (0.870)	0.298 (0.898)	0.389 (0.899)			
NICS(1)	0.365 (0.882)	0.687 (0.884)	0.301 (0.875)	0.391 (0.873)	0.998		
NICS(1)$_{zz}$	0.386 (0.888)	0.687 (0.810)	0.304 (0.878)	0.394 (0.872)	0.998	0.997	
ISE	0.644 (0.955)	0.834 (0.931)	0.593 (0.954)	0.671 (0.956)	0.813	0.809	0.809

[a] The improved correlation coefficients by excluding the most deviated points are given in parenthesis.

Table 9
Correlation coefficients between the used aromaticity indices and the parameters of electron density function at RCP for the considered hepta-fulvene derivatives.[a]

	SA	EN	GEO	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ISE
ρ	0.162	0.077	0.180	0.181	0.038	0.052	0.044	0.558
G	0.395	0.313	0.411	0.434	0.202	0.217	0.211	0.345
V	0.295	0.221	0.309	0.325	0.137	0.149	0.148	0.229
H	0.525	0.458	0.541	0.578	0.316	0.332	0.313	0.562
	(0.814)	(0.831)	(0.822)	(0.828)	(0.831)	(0.869)	(0.783)	(0.834)

[a] The improved correlation coefficients for total electron energy density (H) by excluding the most deviated points are given in parenthesis.

predict the **3w** (R=NN$^+$) as the most aromatic compound among the considered hepta-fulvene derivatives, while these indices do not give consistent results among themselves for the hepta-fulvenes with electron donating substituents. Different NICSs predict **3u** as the most anti-aromatic, whereas ISE index proposed that it is **3i**, and both HOMA and SA predict **3j** as the most non-aromatic system. Also according to the results of this table, the increase in aromaticity of the ring for an electron accepting substituent is more affected by a considerable decrease in bond alternation (GEO). Note that GEO/EN varies from 0.661/0.185 for unsubstituted **3a** to 0.125/0.067 for **3w.** The same effect is observed for GEO term of the systems with electron donating groups. As in the tria- and penta-fulvene derivatives, the calculated SA values for the hepta-fulvene derivatives show an excellent correlation with the GEO contribution of HOMA ($R^2 = 0.991$) rather than the EN part ($R^2 = 0.836$) of this index (see Figs. S5 and S6 in Supplementary materials).

The obtained correlation coefficients between different aromaticity indices for hepta-fulvenes are collected in Table 8. The results show that significant correlations exist between the calculated SA and HOMA index values with $R^2 = 0.993$ (see Fig. 3) and different NICSs among themselves. It should be mentioned that the most deviation in ISE and NICSs with HOMA and SA graphs are observed for the strong electron donating substituents (**3i**, **3j**, **3p** and **3u**). When these compounds are excluded, for the remaining molecules the relationships between these indices are improved. For instance the correlation coefficient of SA vs NICS(0) changes from 0.362 to 0.905. The correlation coefficients for the excluded series are also shown in Table 8.

The evaluated correlation coefficients between the electron density function parameters at RCP (see Table S7 in Supplementary materials) and the other aromaticity indices for the considered hepta-fulvenes are given in Table 9. Again the most deviation is observed for the strong electron donating substituents (**3i**, **3j**, **3p** and **3u**). By excluding these points, the most improvement is observed between the total electron energy density (H) and the other aromaticity indices; while no considerable changes in correlation coefficients are observed for the other electron density parameters.

4. Conclusion

The recently introduced Shannon Aromaticity (SA) index, is used for the prediction of substituent effect on the aromaticity of 70 tria-, penta- and hepta-fulvene mono-substituted derivatives. A comparison is made between the obtained SA values and some other aromaticity indices (HOMA, ISE, NICS(0), NICS(1) and NICS(1)$_{zz}$). It is concluded that although NICS-based indices are not successful in predicting the aromaticity of tria- and hepta-fulvene derivatives, the SA, ISE and HOMA criteria are more reliable for this purpose. It is found that in all cases the obtained SA values show significant correlation with the calculated HOMA index. Since the SA and GEO term of HOMA are both related to the similarity of electron densities in different bonds of a given molecule, a good correlation between these concepts is expected. In all cases a

significant correlation between the GEO contribution of HOMA index and the obtained SA values are observed, which confirm this claim.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2010.12.012.

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