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Global and Local Aromaticity of Linear and Angular Polyacenes

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Abstract—Ab initio (B3LYP/6-311G**) optimisation of seven linear and five angular polyacenes gave us an opportunity to study aromaticity in terms of HOMA index and its components EN and GEO, the energy of the carbon skeleton of these hydrocarbons was calculated from CC bond lengths. Independently, the Cohen–Benson group additivity values were used to estimate the thermochemical aromatic stabilisation energy (ASE). For individual rings the NICS values were computed and compared with HOMA. An increase of size of both linear and angular polyacenes is associated with a substantial decrease in their aromaticity, with a greater decrease for the linear polyacenes. This is well documented by both HOMA and Cohen–Benson ASE. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Benzenoid hydrocarbons belong to the model systems most often employed to study aromatic stability. Their chemical and spectral properties have been subject to extensive studies.[1,2] Benzene was the first compound for which the resonance energy (RE) was determined,[3,4] then RE's of a collection of benzenoids were presented in Wheland's monograph.[5] While the first estimations of the stabilisation energy associated with aromaticity were performed by means of thermochemical methods, in the last few decades much more attention has been paid to quantum chemical methods. After the introduction of Hückel delocalisation energy (DE) which was confusing[6,7] a series of successful works appeared, allowing one to estimate stabilisation energy by the use of simple quantum chemical methods.[7] A dramatic development of computing facilities as well as of theoretical methods, inventing the concepts of isodesmotic[8] and homodesmotic[9] reactions enabled great progress in the computation of aromatic stabilization energies (ASE). Their values, however, depend strongly on the choice of the reference system and the level of theory, leading to a great diversity of the ASE values. For benzene the range between the highest and lowest value of ASE is about 50 kcal/mol.[10]

Recently, benzenoid hydrocarbons have been studied in terms of Bader's Atoms in Molecules model[11] and it was shown that geometry based aromaticity index HOMA[12,13] correlates well with the ring critical point and other electron properties in the ring critical points.[14] Recently it was also shown for some condensed aromatic systems[15] that there exists a good relationship between the electron density at the bond critical point and ellipticity and CC bond length.[15]

The aims of this paper are to analyse interrelations between the aromaticity indices for two series of polyacenes, the linear and angular ones and to establish whether their overall aromatic stabilization depends[7] or not[15] on the number of rings.

Methods

Molecular geometries of seven linear (**1–7**) and five angular (**8–12**) polyacenes (Fig. 1) were optimized (partly based on previous computations[15]) at B3LYP/6-311G** level of theory.[16] For comparison, experimental geometries of three linear (**1–3**)[17–19] and three angular (**8–10**) polyacenes[20–22] with the highest precision of the measurement[23] were retrieved from Cambridge Structural Database.[24]

The obtained geometry was used to estimate geometry-based aromaticity indices: HOMA[12,13] and its components EN and GEO,[25,26] which describe a decrease in aromaticity due to bond elongation and an increase in bond alternation, respectively.

$$\begin{aligned} \mathrm{HOMA} &= 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \\ &= 1 - \left[\alpha(R_{\mathrm{opt}} - R_{\mathrm{av}})^2 + \frac{\alpha}{n}\sum(R_{\mathrm{av}} - R_{\mathrm{i}})^2\right] \\ &= 1 - \mathrm{EN} - \mathrm{GEO} \qquad (1) \end{aligned}$$

Eq. (1) was used to calculate HOMA, where n is the number of bonds taken into the summation and α is an empirical constant chosen to give HOMA=0 for the hypothetical Kekule structures of the aromatic systems (with the lengths

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Keywords: aromaticity; polyacenes; Cohen–Benson ASE, NICS, HOMA.

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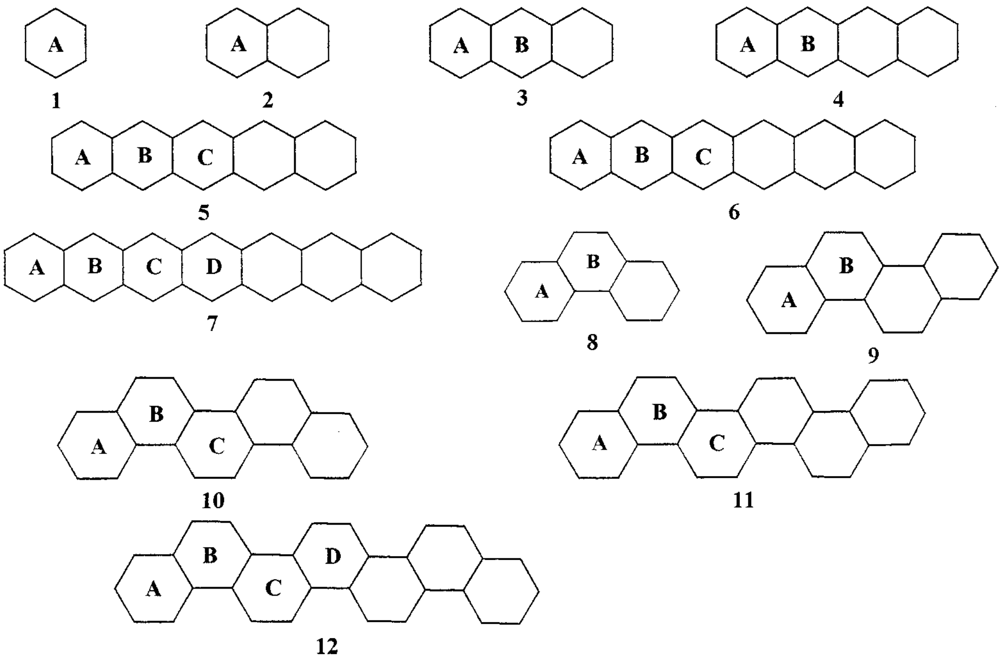


Figure 1. Linear (**1**–**7**) and angular (**8**–**12**) polyacenes studied in this paper. The capital letters label the rings.

for CC bonds as in acyclic polyene, 1,3-butadiene,[27]) and 1 for the system with all bonds equal to the optimal value R_{opt}. The individual bond lengths are depicted by R_{i}. The quantity R_{opt} is defined as a length of the CC bond for which the energy (estimated by use of the harmonic potential) of the compression to the length of a double bond and expansion to the length of single bonds in 1,3-butadiene is minimal.

Another geometry-based index of aromaticity is an estimation of energy calculated from CC-bond lengths. Applying the reference bond lengths and bond energies to the single and double bonds, one obtains an expression for the bond energy, $E(R)$, calculated directly from the bond length:[28]

$$E(n) = 87.99 \exp\{2.255[1.533 - R(n)]\} \qquad (2)$$

where $E(n)$ is an energy of the nth bond with the length $R(n)$. Summation over the bonds which form the ring leads to the ring energy content (REC) and summation over the whole molecule leads to the molecule energy content (MEC).[29] Eq. (2) was tested on heats of formation (from atoms) of eight well measured benzenoid hydrocarbons and the agreement between the experimental and theoretically obtained values was less than 1%.[28] The values used in this report are REC and MEC divided by the number of CC bonds.

The Cohen and Benson method[30] of estimation of the heats of formation from the group additivity values (GAV) is employed to determine Aromatic Stabilisation Energies (ASE) from the calorimetric data. There are three kinds of carbon atom in the hydrocarbons considered in this report which are represented by only two kinds in the olefinic hydrocarbons. The GAV's of these cases are given in Table 1.

The ASE values are designated by E (Table 2) and are calculated as the difference between GAV's for the aromatic system and GAV's for the olefinic one,[15b] divided by the number of π-electrons.

Table 1. The Cohen–Benson group additivity values for conjugated olefins and for aromatic systems. C_d, C_B and C_{BF} specify the doubly bonded carbon atom, carbon atom in a benzene ring and the carbon atom at the junction of two rings, respectively[30]

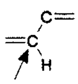
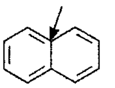
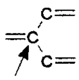
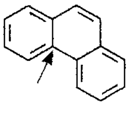
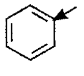
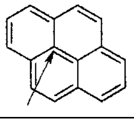
Type of increment	Description	Value	Type of increment	Description	Value
C_d–$(C_d)(H)$		6.78	C_{BF}–$(C_{BF})(C_B)_2$		5.53
C_d–$(C_d)_2$		4.6	C_{BF}–$(C_{BF})_2(C_B)$		4.34
C_B–(H)		3.29	C_{BF}–$(C_{BF})_3$		−0.54

Table 2. Aromaticity indices HOMA, EN, GEO, *E* and MEC/*n* calculated as global values (for whole molecules) for **1**–**12**. Data in brackets are based on experimental geometries

System	HOMA	EN	GEO	E	MEC/*n*
1	0.991 (0.974)	0.009 (0.026)	0.000 (0.000)	3.49	120.4 (119.3)
2	0.811 (0.827)	0.064 (0.036)	0.125 (0.136)	2.61	117.9 (118.9)
3	0.718 (0.710)	0.092 (0.041)	0.190 (0.249)	2.23	117.2 (118.9)
4	0.668	0.115	0.217	2.02	116.6
5	0.628	0.133	0.239	1.88	116.2
6	0.629	0.137	0.234	1.79	116.1
7	0.624	0.145	0.231	1.72	115.9
8	0.741 (0.750)	0.091 (0.005)	0.168 (0.245)	2.40	117.2 (121.1)
9	0.710 (0.658)	0.112 (0.036)	0.178 (0.306)	2.28	116.6 (119.2)
10	0.685 (0.720)	0.132 (0.065)	0.183(0.215)	2.21	116.2 (118.0)
11	0.677	0.135	0.188	2.16	116.1
12	0.668	0.189	0.142	2.12	115.9

Table 3. Correlation coefficients and significance levels (in parentheses) of regressions between HOMA, EN, GEO, ASE/*n* (*E*) and MEC/*n* calculated for whole molecules

	HOMA	EN	GEO	E
EN	−0.892 (0.000)			
GEO	−0.948 (0.000)	0.701 (0.011)		
E	0.989 (0.000)	−0.847 (0.001)	−0.962 (0.000)	
MEC/*n*	0.976 (0.000)	−0.939 (0.000)	−0.877 (0.000)	0.945 (0.000)

Finally, the Nucleus Independent Chemical Shift (NICS)[31] was used as a descriptor of aromaticity from the magnetic point of view. The NICS — defined as a negative value of the absolute shielding[32] was computed[16] at the ring centres and 1 Å above ring centres (NICS(1)) at HF/6-31+G* level of theory using the GIAO method. Within the model assumptions the aromatic rings are those rings with negative values of NICS. The more negative the index, the more aromatic the system.

Table 2 presents all the data for compounds **1**–**12**.

When the whole-molecule aromaticity indices are concerned: HOMA, EN, GEO, MEC/*n* and Cohen–Benson *E*, it is clear that aromaticity of these systems vary monotonically with the increase of the number of rings. This tendency is observed for both series, however with different sensitivity, which is in line with the observation of the changes of the position of p-band in the UV spectra of arenes.[15] The aromaticity of the linear polyacenes is smaller than the corresponding angular systems and moreover it decreases more rapidly with an increase in the size of the system. This tendency is clearly shown by *E* and HOMA. In the frame of the Cohen–Benson model,[30] the *E* value for the linear system with an infinite number of rings is 1.28 whereas for the angular one it is 1.89. This tendency is roughly in line with a decrease in chemical stability of Acenes.[32,33] Evidently the above observation is followed

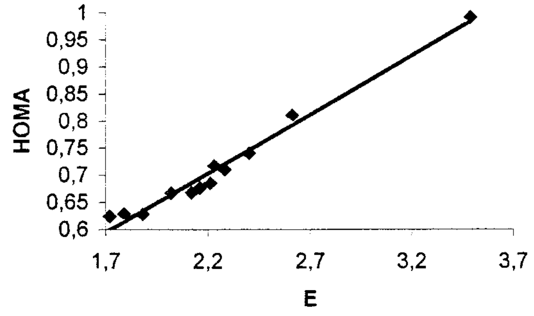


Figure 2. Linear dependence of HOMA index of Cohen–Benson ASE/*n*. Correlation coefficient r=0.989.

Table 4. Aromaticity indices HOMA, EN, GEO, NICS, NICS (1) and BE for individual rings

System	Ring	HOMA	EN	GEO	REC/*n*	NICS	NICS(1)
1	**A**	0.991	0.009	0.000	120.4	−10.5	−12.3
2	**A**	0.787	0.083	0.130	117.2	−10.4	−12.4
3	**A**	0.632	0.123	0.245	116.4	−8.7	−11.0
3	**B**	0.723	0.161	0.116	115.5	−13.5	−15.1
4	**A**	0.539	0.150	0.310	115.9	−7.1	−9.7
4	**B**	0.632	0.207	0.191	114.6	−13.4	−15.0
5	**A**	0.453	0.174	0.373	115.5	−5.8	−8.6
5	**B**	0.574	0.227	0.174	114.2	−12.4	−14.2
5	**C**	0.608	0.237	0.155	114.1	−14.6	−16.1
6	**A**	0.460	0.170	0.370	115.6	−5.0	−7.9
6	**B**	0.528	0.245	0.227	114.1	−11.2	−13.2
6	**C**	0.543	0.261	0.196	113.8	−14.5	−16.1
7	**A**	0.444	0.176	0.379	115.5	−4.3	−7.3
7	**B**	0.505	0.253	0.242	114.0	−10.2	−12.4
7	**C**	0.517	0.275	0.208	113.6	−13.9	−15.5
7	**D**	0.513	0.281	0.206	113.5	−15.2	−16.6
8	**A**	0.870	0.053	0.077	118.2	−10.7	−12.6
8	**B**	0.458	0.289	0.252	113.4	−6.7	−9.6
9	**A**	0.850	0.057	0.093	118.1	−10.5	−12.5
9	**B**	0.568	0.200	0.537	114.3	−7.9	−10.6
10	**A**	0.845	0.063	0.092	117.9	−10.4	−12.4
10	**B**	0.544	0.248	0.209	114.0	−7.3	−10.1
10	**C**	0.669	0.183	0.147	115.1	−8.9	−11.4
11	**A**	0.856	0.055	0.088	118.2	−10.4	−12.4
11	**B**	0.559	0.237	0.207	114.2	−7.4	−10.2
11	**C**	0.643	0.192	0.164	114.9	−8.4	−11.0
12	**A**	0.856	0.055	0.088	118.2	−10.4	−12.4
12	**B**	0.553	0.240	0.208	114.2	−7.3	−10.1
12	C	0.659	0.185	0.155	115.0	−8.5	−11.0
12	**D**	0.618	0.207	0.175	114.7	−7.9	−10.4

Table 5. Correlation coefficients and significance levels (in brackets) of regressions between HOMA, EN, GEO, REC/*n*, NICS and NICS(1) calculated for 14 rings in 5 angular polyacenes (**8**–**12**)

	HOMA	EN	GEO	REC/*n*	NICS
EN	−0.993 (0.000)				
GEO	−0.662 (0.010)	0.579 (0.030)			
REC/*n*	0.989 (0.000)	−0.992 (0.000)	−0.644 (0.013)		
NICS	−0.994 (0.000)	0.992 (0.000)	0.618 (0.018)	−0.982 (0.000)	
NICS (1)	−0.989 (0.000)	0.987 (0.000)	0.606 (0.022)	−0.974 (0.000)	0.998 (0.000)

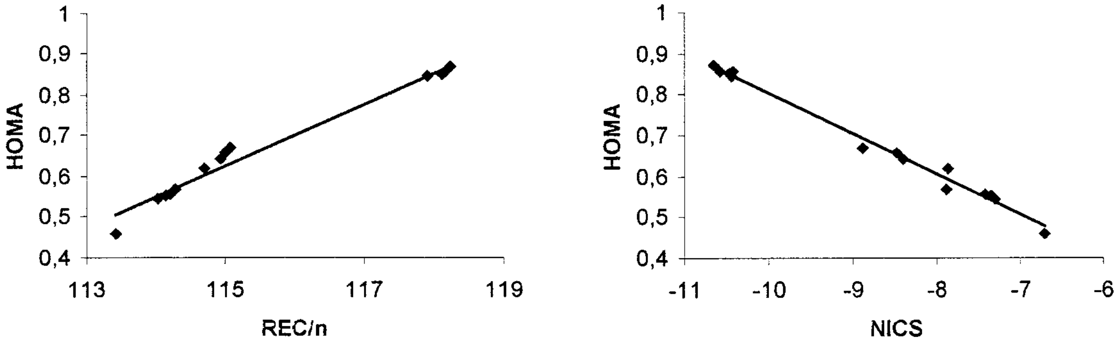


Figure 3. Linear dependencies of HOMA index of REC/*n* and NICS.

by the mutual linear relationships between the above-mentioned indices, as shown by the statistical data of Table 3.

The best correlation between HOMA and ASE/*n* (*E*) was found. This dependence is shown in Fig. 2.

Analysis of individual rings from these 12 arenes leads to a less clear picture. Table 4 presents the results for individual rings.

Both HOMA and NICS clearly show that central rings in linear acenes are more aromatic than the outer ones. Moreover, the aromaticity of the outer rings decreases rapidly with increasing number of rings down to 0.454 (HOMA) and −7.3 (NICS) for heptacene. The NICS, and especially NICS(1), shows that the aromaticity of the central rings increases with the increase of the number of rings in the system and is the highest (−16.6) for the central ring of heptacene. The HOMA follows a slightly different tendency. It also shows the highest aromatic character for the central ring but generally, the aromaticity of the central fragment decreases going from the smaller to the larger system. Interestingly, REC/*n* shows a different picture. Its value for the central rings simultaneously decreases with the number of rings in the system. A rather weak correlation between REC/*n* and HOMA (correlation coefficient r=0.762) is clearly due to the different picture, all other aromaticity descriptors do not depend on each other.

In the case of angular polyacenes the picture is much more comprehensive. All the indices show that the outer rings are most aromatic whereas the central ones vary commutatively in their aromatic character. All the descriptors correlate very well as shown in Table 5. The HOMA index correlates best with REC/*n* (correlation coefficient r=0.989) and with NICS (correlation coefficient r=0.994). Fig. 3 shows these dependences.

The differences in aromatic character of the linear and angular polyacenes shown in this report are in line with the conclusions given in other papers.[15,34] The intensive global energetic parameter based on Cohen and Benson ASE/*n* (*E*) correlates very well with the geometry based index HOMA estimated for the whole molecules and this provides strong support for the statement that the aromaticity of both families of benzenoid hydrocarbons decreases with an increase in the number of rings. This result supports strongly the older view[7] on this matter and is contrary to the results by Wiberg[15] based on a smaller sample of compounds and different methodology. Our observation is also in line with reactivity trends for these systems[1] and hence both families of hydrocarbons may be good examples for fully aromatic systems[10] in which an increase in molecular size is associated with a substantial decrease of all (studied) aromaticity descriptors. Interestingly, for local aromatic character, three independent indices of aromaticity could be applied: the geometry based HOMA, the energetic one, REC, and a magnetic index NICS.[31] The mutual correlations between them for the angular polyacenes are very high as shown by the data in Table 5, whereas this is not the case for the linear polyacenes.

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