Aromatic Character of the Benzene Ring Present in Various Topological Environments in Benzenoid Hydrocarbons. Nonequivalence of Indices of Aromaticity

Tadeusz Marek Krygowski* and Arkadiusz Ciesielski

Department of Chemistry, University of Warsaw, 02 093 Warsaw, ul.Pasteura 1, Poland

Clive William Bird and Andras Kotschy

Department of Chemistry, King's College London, The Strand, London WC2R 2LS, U.K.

The precise geometry of 154 benzene rings embedded in various topological environments of 32 benzenoid hydrocarbons was used for estimating five different indices of aromaticity, namely I_6, HOMA, BAC, BE, and LB. Two of these indices are new: BAC measures the degree of alternation of the bond lengths in the ring, and BE is the bond energy of the ring estimated from the bond lengths using a new interpolation formula. The latter formula satisfactorily reproduces the experimental heats of formation from atoms of a number of benzenoid hydrocarbons. Application of regression and factor analyses to the above mentioned set of data lead to the conclusion that about 70% of the total variance may be explained by energetic indices and only about 25% by the geometric ones. A theoretical index of aromatic character (Randić), based on purely topological patterns of the ring in molecules, correlates much better with energetic indices than with geometrical ones.

INTRODUCTION

Not since the beginning of its use has the term "aromatic character" been clearly defined. Kekulé[1] defined it as being a characteristic of those molecules which contain a benzene ring, i.e., on the basis of the structural pattern of the molecule. Erlenmayer[2] considered aromatic character as "behaving like benzene derivatives". Since then there has been a dichotomy in the understanding of this term. A century later in the 1960s and 1970s it had been more or less generally accepted that aromatic character is associated with[3,4]

(i) a higher stability of the system,

(ii) an averaging of bond lengths, and

(iii) specific magnetic properties (NMR spectral properties).

These properties were claimed to be due to the π-electron delocalization and have been considered as more or less equivalent. Recent quantum chemical studies have shown that it is not the π-electrons which determine directly the stability of the molecule.[5,6] Moreover, recent studies employing principal component analysis[7] revealed that the above mentioned properties are not equivalent indicators of aromatic character.[8,9] Both of these studies were carried out on hetero-π-electron systems with benzene as the only representative of carbocyclic aromatics. In one study the aromaticity indices were of purely theoretical origin,[9] and in the other a mixture of theoretical and experimental indices were used.[8] The lack of complete data for some of the systems under consideration led to some incompleteness of the data matrices. Both sets of workers concluded that aromaticity is a multidimensional phenomenon. However, Katritzky et al. found that three principal components were required to account for 83% of the total variance of the data matrix,[8] while Jug and Köster found that 75% of the total variance of their data set could be explained by only two principal components.[9] Undoubtedly from these results it may be concluded that aromaticity is a multidimensional

phenomenon, but the question may be posed as to whether this is a consequence of using too much of a heterogeneous sample for statistical examination, or is it an inherent property of π-electron systems virtually independent of sampling. It could perhaps be due to the well-known weaknesses of theoretical calculations if conducted for excessively heterogeneous molecular systems, with very different hetero atoms and hence problems of parameterization.

To answer these questions we have undertaken an investigation of the aromatic character of the benzene ring embedded in various topological environments in polycyclic benzenoid hydrocarbons. In this way we expect to maintain the homogeneity of the sample studied. In contrast to both of the studies cited above we have used only indices derived from the bond lengths of molecules obtained by X-ray, neutron, or electron diffraction. Apart from some already estabilished indices of aromaticity, we present some others which are also based on experimentally determined molecular geometry and can be considered as geometrical, energetic, or magnetic. Overall this provides a satisfactory range of experimentally based criteria for our investigation.

AROMATICITY INDICES USED IN THIS STUDY

Most of the well-known indices of aromaticity have been surveyed in the aforementioned papers[8,9] where they have been used in the principal component analysis of aromatic character. Hence we shall only recall here those used in this study and present some new ones.

The I_6 index[10] is defined as

$$I_6 = 100 \, (1 - V/33.3) \tag{1}$$

where

$$V = \frac{100}{N_{av}} \sum (N_n - N_{av})^2$$

and the bond orders N are given by $(a/R^2 - b)$. R is the bond length, and a and b are empirical constants. The HOMA index for hydrocarbons is defined as[11]

$$\text{HOMA} = 1 - \{a\sum_i^n (R^{\text{opt}} - R_i)^2\}/N \qquad (2)$$

where R^{opt} is an empirically estimated optimal bond length equal to 1.388 Å for CC bonds which is assumed to be realized when full delocalization of π-electrons occurs, a is an empirical constant[12] dependent on the kind of the bond (equal to 157.7 for CC bonds), and R_i stands for the bond lengths taken into account.

By analogy to the Jug[13] bond order approach to ring current we accept that the "magnetic type" index of aromaticity is depicted by the longest bond length in the π-electron system under consideration. Thus, the Jug RC index,[13] i.e. the lowest value of the bond order in the ring, is now termed as LB and defined as LB = maximum bond length.

Following the double bond fixation theory[14] we propose now a new, purely geometrical index of aromaticity called the bond alternation coefficient, BAC, defined as

$$\text{BAC} = \sum_r (R_r - R_{r+1})^2 \qquad (3)$$

where R_r and R_{r+1} are consecutive bond lengths in the ring and summation runs over all bonds of the molecule or the fragment under study (benzene rings in the present case). This index is reminiscent of that proposed by Pozharski.[15]

Another newly suggested index is simply the sum of the bond energies of the molecular fragment in question. These energies are obtained from the interpolation formula

$$\text{BE} = E(1)\exp[\alpha\{R(1) - R(n)\}] \qquad (4)$$

where $R(1)$ and $R(n)$ are the respective bond lengths of a single bond and the bond in question, and α is an empirical constant. Consequently, the energy of a given fragment (or for the whole molecule) is given by summation over all the bonds in question, i.e.,

$$\text{BE(molecule or its fragment)} = \sum_{i=1}^{N}(\text{energy}(i)) \qquad (5)$$

Of these two new indices the former, BAC, is a conceptual consequence of the double bond fixation theory,[14] but the validity of the latter one BE may be verified by comparison of the calculated energies for a series of compounds with independently obtained experimental values. As the accuracy of the final results depends upon the derivation of the empirical formula a more detailed presentation is appropriate.

DERIVATION AND VALIDATION OF THE BOND ENERGY FORMULA

More than 40 years ago Pauling[17] defined a fractional bond number, n, in terms of the difference between the interatomic distance (bond length), $R(n)$, and a standard "single bond" length $R(1)$, as given by the expression

$$R(n) - R(1) = -c\ln n \qquad (6)$$

where c is an empirical constant. The usefulness of this idea in structural chemistry has been demonstrated[18] in recent years. Another empirical rule[19] relates the bond energy $E(n)$ to the bond number n

$$E(n) = E(1)n^p \qquad (7)$$

where $E(1)$ and $E(n)$ represent the energies of bonds with bond numbers equal to 1 and n, respectively.

The combination of eq 6 and 7 leads to the formula for the bond energy $E(n)$

$$E(n) = E(1)\exp\{\alpha[R(1) - R(n)]\} \qquad (8)$$

where $\alpha = p/c$. We note that this equation is similar to the old empirical formula relating bond energy to bond length employed in semiempirical methods of quantum chemistry[20]

$$\beta(\text{XY}) = \beta_0\exp(-g\Delta R)$$

where $\beta(\text{XY})$ is the HMO resonance integral for the π-electrons of the bond and β_0 the reference value. The parameter g is empirically derived, whereas ΔR is the difference between the XY bond length and that of some reference bond.

Initially we used the following reference bond lengths and energies for calculating BE:

$$R(1) = 1.533 \text{ Å}^{21} \qquad (9a)$$

$$R(2) = 1.337 \text{ Å}^{22} \qquad (9b)$$

$$E(1) = 94.66 \text{ kcal/mol}^{23} \qquad (9c)$$

$$E(2) = 132.91 \text{ kcal/mol}^{23} \qquad (9d)$$

Substitution of these data into the general formula 8 provided a numerical formula for calculating bond energies for carbon—carbon bonds from bond lengths. In order to obtain energies directly comparable to experimentally accessible quantities such as heats of formation, it is necessary to take into account the energies of CH bonds. As CH bond lengths are not available from X-ray diffraction experiments with sufficient precision, we assumed that each bond could be treated as having an additive energy equal to 100.53 kcal/mol.[23] Addition of CH bond energies to the energies calculated for the CC bonds from their lengths gave heats of formation from atoms for a number of hydrocarbons not too far distant from the experimental values. In view of the considerable debate[23] as to the appropriate value for $E(\text{CC})$ in such situations we selected a value of 87.99 kcal/mol, which reproduces the establiished heat of formation from atoms of benzene, 1320.6 kcal/mol, when used in conjunction with the CC bond length of 1.397 Å for benzene obtained from microwave measurements[24] and low temperature neutron diffraction.[25] The revised equation is

$$E = 87.99\exp\{2.255[1.533 - R]\} \qquad (10)$$

Thus for any benzenoid hydrocarbon the formula for calculating the heat of formation from atoms (HtFfA) from CC bond lengths becomes

$$\text{HtFfA} = -100.53n - 87.99\sum_{i=1}^{N}\exp\{2.255(1.533 - R_i)\} \qquad (11)$$

BENZENOID HYDROCARBONS

J. Chem. Inf. Comput. Sci., Vol. 35, No. 2, 1995 **205**

Table 1. Comparison of Heats of Formation for Hydrocarbons Calculated by Eq 11 with Experimental Values[55]

compound	estimated HtFfA	experimental HtFfA
benzene	1320.6	1320.6
naphthalene	2100.8	2093.8
anthracene	2868.4	2863.9
phenanthrene	2861.8	2869.5
tetracene	3592.4	3638.8
chrysene	3664.4	3643.9
triphenylene	3647.3	3641.2
3,4-benzophenenthrene	3646.6	3638.8
pyrene	3227.8	3207.7

where n is the number of CH bonds in the molecule and the summation in (11) is over all N CC bonds.

The application of this formula to eight benzenoid hydrocarbons of well established geometry gave the results presented in Table 1. The estimated mean error for the calculated heats of formation, HtFfA, is 26.5 kcal/mol which is less than 1% of the mean value of HtFfA. Two factors should be borne in mind in assessing the relatively good agreement between experimental heats of formation and those estimated by eq 11.

Firstly experimentally determined bond lengths are not always of good accuracy and precision. For example the X-ray CC bond length in benzene with correction for libration is 1.392 Å,[26] which leads to an estimated HtFfA for benzene of 1328.7 kcal/mol, whereas the geometry estabilished by Stoicheff[24] and Jeffrey et al.[25] reproduces, by definition the experimental value of 1320.6 kcal/mol. This kind of discrepancy may become even larger for bigger molecules.

Secondly, in our procedure we accepted of neccessity that the energy of CH bond is an additive and constant term, although it is well-known that neither CH bond length nor energy are constant.[27,28] This may be a source of error which could increase with the increasing number of CH bonds in the molecule. However, this is not relevant to its use in the present paper which is concerned solely with C_6 fragments.

Overall these results are sufficiently encouraging to apply the procedure in studies such as the present where formula 11 enables the calculation of heats of formation from atoms for molecular fragments.

RESULTS AND DISCUSSION

We have estimated the above presented aromaticity indices for 154 benzenoid rings observed in 32 benzenoid hydrocarbons whose molecular geometries were listed in the Cambridge Structural Database[29] (release April 1992). Only compounds with average estimated standard deviations for CC bonds ≤0.010 Å and an R factor less than 0.07 were used in this study. When the geometry of the compound was determined by more than one research group, then we have employed all of them subject only to the recorded precision of the determination. The numerical results for all of the above mentioned indices derived from the original geometries are listed in Table 2. These data were then analyzed by regression and factor analyses.

Regression Analysis. All of the aromaticity indices mentioned above have been plotted one against another providing the correlation coefficients listed in Table 3. These are rough data and take into consideration all data without

any corrections. It is immediately clear that the indices are not equivalent even for such a homogeneous sample as benzene rings differing only in their topological environment in benzenoid hydrocarbons. This is qualitatively in line with former conclusions.[8,9] Nevertheless some of the indices are relatively well correlated, and others not so as seen in Figure 1. The best correlated pairs are I_6 and BAC (−0.937) and HOMA and LB (−0.909), but both with negative correlation coefficients. The first case is easily understood since the higher is the value of I_6, i.e., aromatic character of the ring, the lower is the BAC value, i.e., alternation of bond lengths, and is entirely in accord with expectation. Similarly in the second case, the higher is the HOMA value, i.e., aromatic character of the ring, the shorter is the longest bond (LB value). This is in accord with the definition of this index since increasing aromaticity should result in an accompanying decrease in alternation of bond lengths as their values approach the optimal bond length.[12]

These two plots differ slightly from one another. The first one, I_6 vs BAC ($R = 0.937$), has fewer outliers than the other one, HOMA vs LB ($R = -0.909$) which contains more substantial outliers. Very unexpectedly the geometrically defined index LB correlates better with energetical indices (BE, HOMA) than purely geometrical ones (BAC or I_6). This finding needs further study with a wider range of systems taken into analysis.

It is apparent from the data of Table 3 that indices of aromaticity may be grouped into two classes; one consisting of I_6 and BAC and the other of HOMA, BE, and LB. The first class may be viewed as geometric indices since BAC is a direct measure of the alternation of the bond lengths, which in turn is a measure of the nonaromatic character of the system. The other class must be viewed as an energetic measure of aromaticity since BE is the energy of the ring. Very unexpectly the geometrically defined index LB correlates better with energetical indices (BE, HOMA) than with purely geometrical ones BAC (or I_6). This finding needs further study taking into account a wider range of systems.

On adding the squared correlation coefficients in the columns of Table 3, i.e., R^2, an approximate measure of strength of interrelation of a given index with all remaining ones is obtained. The highest value of $\sum R^2$ is found for HOMA (2.288) and then for LB (2.077). This indicates that among the indices considered these two are most "pluralistic" that is the best correlated with all of the other ones. The most selective is I_6 (1.202). It may be concluded, as shown by values for these parameters, that energetic indices are less selective in respect of various contributions related to the aromatic character.

If we take into account the next best two correlations, HOMA vs BE ($R = 0.831$) and LB vs BE ($R = 0.802$), the conclusion is reached that all of the indices correlated by these two regressions belong to the energetic index group. Moreover for both scatterplots the outliers are dispersed on one side of the regression line. Detailed analysis of the outliers for these four scatterplots does not lead to any indication of structural regularity.

All of the scatterplots for which Table 2 gives the statistical parameters are presented in Figure 1.

Factor Analysis. Treatment of all of the data of Table 2 by means of factor analysis[9,30] provides the results given in Table 4. It is immediately clear that only two factors are

Table 2. Aromaticity Indices for Individual Benzenoid Rings[a]
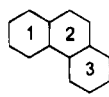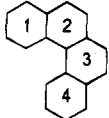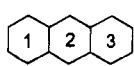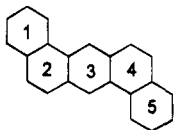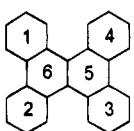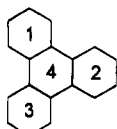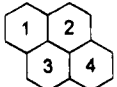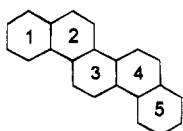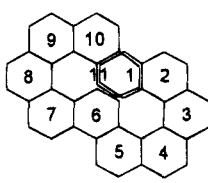
no.	HOMA	BAC	I_6	BE	LB	esd	ring	
1	1.000	0.000	100.0	717.4	1.397	A	1	benzene[25]
2	0.994	0.005	98.9	724.6	1.395	A	1	
3	0.814	0.082	82.2	709.5	1.423	A	1,2	naphthalene[32,33]
4	0.802	0.088	81.3	709.3	1.424	A	1,2	
5	0.809	0.084	81.9	709.3	1.423	A	1,2	
6	0.805	0.086	81.3	709.9	1.424	A	1,2	
7	0.823	0.084	81.7	711.7	1.423	A	1,2	
8	0.821	0.088	80.6	714.1	1.424	A	1,2	
9	0.882	0.078	82.3	725.2	1.425	B	1	phenanthrene[34]
10	0.400	0.173	64.0	699.4	1.456		2	
11	0.898	0.052	84.9	719.5	1.441		3	
12	0.891	0.035	88.4	711.5	1.421	B	1	
13	0.350	0.159	67.2	690.2	1.465		2	
14	0.953	0.042	91.1	719.6	1.441		3	
15	0.859	0.068	81.0	723.4	1.424	B	1	benzophenanthrene[35]
16	0.507	0.132	67.8	700.2	1.446		2	
17	0.499	0.127	68.5	699.1	1.460		3	
18	0.817	0.100	77.7	723.6	1.418		4	
19	0.624	0.127	72.6	705.2	1.446	A	1,3	anthracene[36,37]
20	0.839	0.039	92.3	701.5	1.423		2	
21	0.638	0.116	74.5	702.4	1.437	A	1,3	
22	0.763	0.066	86.8	698.5	1.436		2	
23	0.608	0.135	71.0	706.7	1.448	A	1,3	
24	0.742	0.089	81.8	701.5	1.427		2	
25	0.830	0.067	78.9	723.1	1.420	B	1,5	dibenzoanthracene[38]
26	0.425	0.138	69.1	691.8	1.458		2,4	
27	0.874	0.060	88.1	709.4	1.425		3	
28	0.881	0.063	83.2	720.8	1.421	B	1	dibenzochrysene[39]
29	0.843	0.086	80.6	719.0	1.429		2	
30	0.924	0.056	86.0	724.8	1.414		3	
31	0.895	0.064	83.5	724.5	1.416		4	
32	0.348	0.131	76.5	679.5	1.475		5	
33	0.314	0.126	75.8	678.3	1.467		6	
34	0.936	0.057	87.8	722.5	1.411	B	1	triphenylene[40]
35	0.962	0.028	92.3	720.2	1.409		2	
36	0.912	0.048	86.8	718.5	1.422		3	
37	0.077	0.148	73.4	668.9	1.478		4	
38	0.880	0.039	86.9	711.9	1.425	A	1	pyrene[41]
39	0.572	0.126	73.2	697.2	1.438		2	
40	0.572	0.119	73.5	696.5	1.435		3	
41	0.886	0.093	86.8	713.2	1.424		4	
42	0.926	0.064	85.8	728.8	1.409	B	1	picene[42]
43	0.552	0.142	70.7	704.4	1.478		2	
44	0.764	0.091	83.5	701.8	1.434		3	
45	0.667	0.106	75.3	705.4	1.458		4	
46	0.808	0.078	78.0	719.4	1.426		5	
47	0.867	0.074	81.7	738.8	1.410	B	1	diphenanthropicene[43]
48	0.482	0.145	64.9	706.4	1.462		2	
49	0.458	0.146	62.1	709.7	1.451		3	
50	0.415	0.137	63.6	701.8	1.451		4	
51	0.444	0.167	65.4	703.0	1.459		5	
52	0.729	0.107	77.1	707.5	1.438		6	
53	0.585	0.131	68.1	708.5	1.442		7	
54	0.371	0.162	62.2	699.9	1.460		8	
55	0.620	0.119	71.6	705.8	1.449		9	
56	0.490	0.150	64.9	705.8	1.453		10	
57	0.855	0.079	80.0	727.2	1.419		11	

BENZENOID HYDROCARBONS

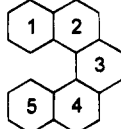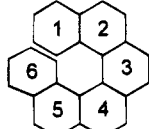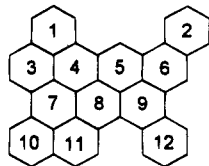*J. Chem. Inf. Comput. Sci., Vol. 35, No. 2, 1995* **207**

Table 2 (Continued)

no.	HOMA	BAC	I_6	BE	LB	esd	ring	
58	0.816	0.075	80.2	711.7	1.431	A	1	perylene[44]
59	0.820	0.097	80.2	721.9	1.428		2	
60	0.133	0.084	82.9	648.1	1.471		3	
61	0.799	0.081	78.5	713.5	1.429		4	
62	0.812	0.074	79.4	713.4	1.429		5	
63	0.782	0.101	76.4	717.4	1.426	B	1	tetrabenzoperylene[45]
64	0.682	0.069	82.5	695.6	1.449		2	
65	0.271	0.126	77.5	674.7	1.473		3	
66	0.879	0.069	82.1	725.2	1.424		4	
67	0.810	0.022	94.9	697.6	1.425		5	
68	0.862	0.075	80.6	727.6	1.420		6	
69	0.264	0.117	78.9	673.3	1.474		7	
70	0.337	0.086	80.9	675.3	1.462		8	
71	0.884	0.057	82.9	721.8	1.416		9	
72	0.862	0.082	80.8	723.8	1.418	A	1	pentahelicene[46]
73	0.510	0.137	66.9	703.1	1.455		2	
74	0.573	0.126	69.5	703.9	1.443		3	
75	0.427	0.152	64.2	700.5	1.455		4	
76	0.833	0.094	78.6	724.8	1.417		5	
77	0.830	0.088	78.0	728.8	1.415	B	1	hexahelicene[47]
78	0.404	0.168	61.7	704.9	1.455		2	
79	0.404	0.173	59.2	711.2	1.447		3	
80	0.570	0.136	67.2	709.2	1.444		4	
81	0.527	0.136	67.5	702.9	1.440		5	
82	0.837	0.074	80.0	720.3	1.433		6	
83	0.874	0.081	82.5	720.2	1.417	B	1	heptahelicene[48] [b]
84	0.583	0.115	68.8	709.2	1.457		2	
85	0.532	0.144	65.6	707.9	1.439		3	
86	0.659	0.090	74.3	705.7	1.454		4	
87	0.643	0.155	68.8	723.7	1.442		5	
OMITTED							6	
88	0.839	0.070	78.8	729.8	1.415		7	
89	0.780	0.116	74.7	730.5	1.418	B	1	
90	0.681	0.097	76.5	702.2	1.431		2	
91	0.767	0.058	83.6	701.8	1.437		3	
92	0.737	0.076	80.8	703.0	1.446		4	
93	0.573	0.120	69.0	705.2	1.446		5	
94	0.571	0.098	72.5	698.8	1.453		6	
95	0.868	0.086	81.3	725.7	1.426		7	
96	0.873	0.072	81.7	724.6	1.414	B	1	tribenzophenanthrapentaphene[49]
97	0.744	0.085	82.1	701.3	1.435		2	
98	0.639	0.108	74.5	701.3	1.436		3	
99	0.198	0.106	80.1	669.3	1.469		4	
100	0.909	0.066	85.5	720.5	1.412		5	
101	0.742	0.048	90.2	694.1	1.433		6	
102	0.563	0.120	72.0	698.9	1.448		7	
103	0.258	0.128	76.1	675.0	1.461		8	
104	0.952	0.047	88.8	726.4	1.411		9	
105	0.692	0.106	78.1	701.7	1.441		10	
106	0.913	0.058	85.0	724.9	1.413		11	
107	0.896	0.057	83.4	724.3	1.412	B	1	dibenzonaphthopyranthrene[50]
108	0.713	0.141	73.0	719.6	1.439		2	
109	0.490	0.180	64.7	707.7	1.445		3	
110	0.245	0.096	79.2	672.3	1.483		4	
111	0.718	0.133	72.4	724.2	1.443		5	
112	0.645	0.121	74.3	704.0	1.451		6	
113	0.623	0.093	82.3	691.0	1.443		7	
114	0.822	0.048	90.7	701.0	1.443		8	
115	0.172	0.165	61.7	686.7	1.470		9	
116	0.814	0.077	78.0	723.2	1.432		10	
117	0.500	0.141	67.8	699.8	1.443		11	
118	0.872	0.068	81.5	728.2	1.427		12	

Table 2 (Continued)

no.	HOMA	BAC	I_6	BE	LB	esd	ring	
119	0.826	0.050	83.9	708.8	1.432	B	1	anthrabenzonaphthopentacene[51]
120	0.712	0.088	81.0	699.5	1.441		2	
121	0.370	0.147	67.5	689.7	1.454		3	
122	0.889	0.043	86.3	714.2	1.421		4	
123	0.527	0.128	72.5	694.4	1.443		5	
124	0.794	0.059	87.5	700.4	1.427		6	
125	0.603	0.067	87.7	685.8	1.450		7	
126	0.294	0.064	86.8	670.0	1.469		8	
127	0.666	0.111	75.5	702.5	1.434		9	
128	0.723	0.097	77.8	705.4	1.443		10	
129	0.756	0.095	79.5	706.1	1.430		11	
130	0.782	0.085	79.3	710.9	1.434	A	1	quaterrylene[52]
131	0.809	0.080	79.9	713.9	1.429		2	
132	0.138	0.076	84.6	664.3	1.471		3	
133	0.773	0.064	80.7	707.3	1.432		4	
134	0.777	0.059	81.4	706.4	1.432		5	
135	0.250	0.066	86.6	668.0	1.466		6	
136	0.749	0.064	79.7	705.9	1.434		7	
137	0.776	0.070	79.2	709.2	1.431		8	
138	0.189	0.078	84.2	666.6	1.468		9	
139	0.851	0.071	83.9	712.3	1.430		10	
140	0.844	0.083	81.4	716.1	1.421		11	
141	0.601	0.100	78.0	693.2	1.438	A	1,10	ovalene[53]
142	0.816	0.037	91.2	700.0	1.426		2,9	
143	0.314	0.169	63.7	695.0	1.480		3,8	
144	0.491	0.117	71.7	695.5	1.480		4,7	
145	0.728	0.054	86.8	695.2	1.435		5,6	
146	0.759	0.097	74.4	722.6	1.433	B	1	tetrabenzopentacene[54]
147	0.757	0.100	74.7	720.5	1.433		2	
148	0.187	0.112	77.4	670.8	1.476		3	
149	0.609	0.130	68.2	716.7	1.439		4	
150	0.681	0.055	88.9	690.4	1.438		5	
151	0.704	0.100	73.4	715.8	1.440		6	
152	0.103	0.108	78.2	666.5	1.480		7	
153	0.762	0.110	75.4	717.7	1.427		8	
154	0.804	0.089	77.0	722.6	1.422		9	

[a] References are to the sources of molecular geometries. The average estimated standard deviation for CC bonds in any one case is indicated by A (0.001−0.005) or B (0.006−0.010). [b] One of the CC bond lengths in ring 6 has an unacceptable length of 1.293 Å, which is evidently in error.

Table 3. Correlation Coefficients for Individual Pairs of Aromaticity Indices

	BAC	I_6	HOMA	BE	LB
BAC	1.000	—			
I_6	−0.937	1.000			
HOMA	−0.668	0.560	1.000		
BE	−0.253	0.093	0.831	1.000	
LB	0.595	−0.495	−0.909	−0.802	1.000
ΣR_i^2	1.746	1.202	2.288	1.525	2.077

needed to explain 95.8% of the total variation of the data in Table 2. Moreover the first factor accounts for 70.0%. This result is at variance with earlier conclusions,[8,9] where more factors (three) were needed to explain a smaller fraction of the total variation. This in turn supports the suspicion that part of the inconsistency between preceding studies[8,9] may arise from the excessively heterogeneous nature of the π-electron systems selected. When the sample is more homogeneous, as in the present study, the multidimensionality of aromaticity becomes less pronounced.

When the factors $f_1 - f_3$ are rotated, then they may be more effectively correlated with the original data. The weights of the original vectors contributing to the factors are presented in Table 5. It is seen that the factor f_1 accounting 70.0% of the total variation correlates stronger

with BE, HOMA, and LB with respective weights 0.993, 0.863, and −0.826, while weights for the other two indices are much less. The contrary situation occurs with factor f_2, which accounts for 25.8% of the total data variation. Here the weights are much higher for I_6 and BAC, 0.977 and −0.948, respectively, whereas the others are much less, 0.470, −0.014, and −0.374. These results are in line with our earlier conclusions from regression analysis, namely that the aromaticity indices considered in this paper may be classified as either geometrical or energetical.

Comparison with the Randić Index of Benzenoid Character. Randić has introduced a graph theoretical index[31] relating similarity of a given benzene ring to an isolated benzene ring. These indices which are estimated directly from the topology of the benzenoid hydrocarbons have been compared with the aromaticity indices discussed above. These correlations were made using data for 53 rings of 19 polycyclic benzenoid hydrocarbons, and the results are recorded in Table 6. It may be concluded, that the Randić index correlates relatively well with the energetical indices BE and HOMA with coefficients of 0.91 and 0.88, respectively, less well with LB (−0.82) and markedly poorer with BAC (−0.77) and I_6 (0.64). Thus the two independent approaches give relatively convergent conclusions.
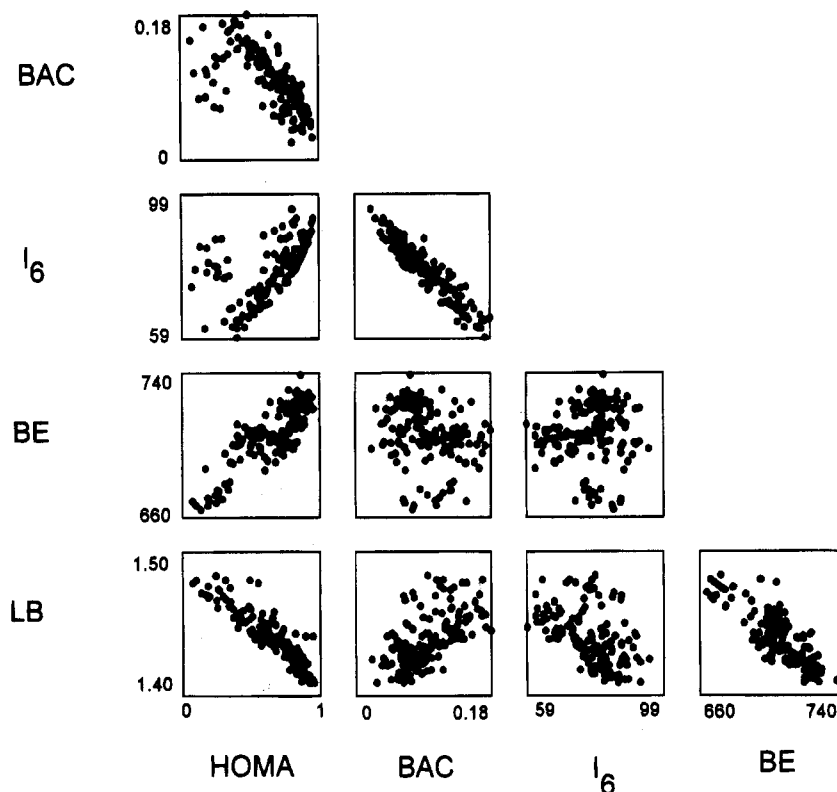
BENZENOID HYDROCARBONS

J. Chem. Inf. Comput. Sci., Vol. 35, No. 2, 1995 **209**

Figure 1.

Table 4. Factor Matrix

variable	f_1	f_2	f_3
HOMA	0.973 38	−0.128 28	0.091 60
BAC	−0.82221	0.53808	−0.08654
I_6	0.73135	−0.66552	−0.00774
BE	0.73106	0.65667	0.14841
LB	−0.92046	−0.26574	0.28442

Table 5. Rotated Factor Matrix

variable	f_1	f_2	f_3
HOMA	0.86563	−0.47004	−0.05008
BAC	−0.27048	−0.94815	0.03002
I_6	0.10833	0.97683	−0.10922
BE	0.99315	−0.00734	0.03606
LB	0.82865	0.37184	0.41693

Table 6. Correlation Coefficients for Individual Aromaticity Indices versus the Randić Index

	HOMA	BAC	I_6	BE	LB
Randić index	0.885	−0.769	0.644	0.911	−0.817

CONCLUSIONS

This investigation demonstrates that even when aromaticity indices are compared for homogeneous systems provided by benzene rings embedded in various topological environments mutual equivalence of indices is not observed. In the case of benzenoid hydrocarbons two factors suffice to account for as much as 95.8% of the total variance. The indices may be grouped into geometrical (I_6 and BAC) and energetical (HOMA, BE, and LB) classes. The energetical indices, BE and HOMA, correlate well with the typical topological Randić index,[31] indicating that the greater part of information relating to the aromatic character of the π-electron system in benzenoid hydrocarbons is already contained in their topology.

REFERENCES AND NOTES

(1) Kekulé, A. Über die Constitution der aromatischen Substanzen. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.

(2) Erlenmayer, E. Studien Über die sogenanten aromatischen Saüren. *Ann. Chem. Pharm.* **1866**, *137*, 327.

(3) Sondheimer, F. The Chemistry of Annulenes. *Pure Appl. Chem.* **1964**, *7*, 363.

(4) *Aromaticity, Pseudoaromaticity and Anti-aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israel Academy of Sciences and Humanities: Jerusalem, 1971.

(5) Shaik S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. Is Delocalization a Driving Force in Chemistry? *J. Am. Chem. Soc.* **1987**, *109*, 363.

(6) Jug, K.; Köster, A. M. Influence of σ and π Electrons on Aromaticity. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

(7) Malinowski, E. R.; Howery, D. G. *Factor Analysis in Chemistry*; Wiley Interscience: 1980; New York.

(8) Katritzky, A. R.; Barczyński, P.; Musumarra, G.; Pisano, D.; Szafran, M. Aromaticity as a Quantitative Concept. 1. A Statistical Demonstration of the Orthogonality of "Classical" and "Magnetic" Aromaticity in Five- and Six-Membered Heterocycles. *J. Am. Chem. Soc.* **1989**, *111*, 7. Katritzky, A. R.; Feygelman, V.; Musumarra, G.; Barczyński, P.; Szafran, M. Aromaticity as a Quantitative Concept. 2. Sixteen Familiar Five- and Six-membered Monocyclic Heterocycles. *J. Prakt. Chem.* **1990**, *332*, 853. Katritzky, A. R.; Feygelman, V.; Musumarra, G.; Barczyński, P.; Szafran, M. Aromaticity as a Quantitative Concept. 3. Benzo-fused Five- and Six-membered Heterocycles. *J. Prakt. Chem.* **1990**, *332*, 870. Katritzky, A. R.; Barczyński, P. Aromaticity as a Quantitative Concept. 4. Less Familiar Five- and Six-membered Monocyclic Heterocycles. *J. Prakt. Chem.* **1990**, *332*, 885.

(9) Jug, K.; Köster, A. M. Aromaticity as a Multi-Dimensional Fenomenon. *J. Phys. Org. Chem.* **1991**, *4*, 163.

(10) Bird, C. W. A New Aromaticity Index and its Application to Five-membered Ring Heterocycles. *Tetrahedron* **1985**, *41*, 1409.

(11) Kruszewski, J.; Krygowski, T. M. Definition of Aromaticity Basing on the Harmonic Oscillator Model. *Tetrahedron Lett.* **1972**, 3842.

(12) Krygowski, T. M. Crystallographic Studies of Inter- and Intramolecular Interactions Reflected in Aromatic Character of π-Electron Systems. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

(13) Jug, K. A Bond Order Approach to Ring Current and Aromaticity. *J. Org. Chem.* **1983**, *48*, 1344.

(14) Binsch, G.; Heilbronner, E. Double Bond Fixation in Non-Alternant π-Electron Systems. *Tetrahedron* **1968**, *24*, 1215.

(15) Pozharski, A. F. *Chem. Heterocycl. Comp.* **1985**, *21*, 717.

(16) Krygowski, T. M.; Kalinowski, M. K.; Turowska-Tyrk, I.; Hiberty, P. C.; Milart, P.; Silvestro, A.; Topsom, R. D.; Daehne, S. Crystallographic Studies of Inter- and Intramolecular Interactions. Part 4. A Comparative Study of the Effect of Through-Resonance on the Geometry of p-Nitro- and p-Nitrosophenolate Anions. *Struct. Chem.* **1991**, *2*, 71.

(17) Pauling, L. Atomic Radii and Interatomic Distances in Metals. *J. Am. Chem. Soc.* **1947**, *69*, 542.

(18) Bürgi, H.-B. Stereochemistry of Reaction Paths as Determined from Crystal Structure Data—A Relationship between Structure and Energy. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 460.

(19) Johnston, H. S.; Parr, Ch. Activation Energies from Bond Energies. I. Hydrogen Transfer Reactions. *J. Am. Chem. Soc.* **1963**, *84*, 2544.

(20) Longuett-Higgins, H. C.; Salem, L. The Alternation of Bond Lengths in Long Conjugated Chain Molecules. *Proc. Roy. Soc.* **1959**, *251A*, 172.

(21) Hedberg, K.; Schomaker, V. The Reinvestigation of the Structures of Diborane and Ethane by Electron Diffraction. *J. Am. Chem. Soc.* **1951**, *73*, 1482.

(22) Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitsu, K.; Young, J. E., Jr. Electron-Diffraction Study of the Structures of C_2H_4 and C_2D_4. *J. Chem. Phys.* **1965**, *42*, 2683.

(23) George, P. A Critique of the Resonance Energy Concept with Particular Reference to Nitrogen Heterocycles, Especially Porphyrins. *Chem. Rev.* **1975**, *75*, 85.

(24) Stoicheff, B. P. *Can. J. Phys.* **1954**, *32*, 334.

(25) Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. The Crystal Structure of Deuterated Benzene. *Proc. Roy. Soc. Ser. A* **1987**, *414*, 47.

(26) Cox, J. D.; Cruickshank, D. W. J.; Smith, J. A. S. Crystal Structure of Benzene: A New Type of Systematic Error in Precision X-ray Crystal Analysis. *Nature* **1955**, *175*, 766.

(27) Furka, A.; Sebastyn, F. Do the C−H Bonds Contribute to the Stabilisation Energy of Benzene? *Croat. Chem. Acta* **1980**, *53*, 555.

(28) Häfelinger, G. *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*; Zalewski, R. I., Krygowski, T. M., Shorter, J., Eds.; Elsevier: Amsterdam, 1991; Chapter 4.

(29) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T. W. A.; Hummelink-Peters, B. G. M. C.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. The Cambridge Crystallographic Data Centre: Computer-Based Search, Retrieval, Analysis and Display of Information. *Acta Crystallogr. Sect. B* **1979**, *35*, 2331. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; McRae, Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. The Development of Versions 3 and 4 of the Cambridge Structural Database System. *J. Chem. Inf. Comp. Sci.* **1991**, *31*, 187.

(30) Donald, F.; Morrison, *Multivariate Statistical Methods*; McGraw-Hill Book Company: English edition copyright 1967; 1976.

(31) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68. Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1989.

(32) Ponomarev, V. I.; Filipenko, O. S.; Atovmyan, L. O. Kristallitcheskaya i Molekularnaja Struktura Naftalina pri −150 °C (in Russian). *Kristallogr.* **1976**, *21*, 392.

(33) Brock, C. P.; Dunitz, J. D. Temperature Dependence of Thermal Motion in Crystalline Naphthalene. *Acta Crystallogr. B* **1982**, *38*, 2218.

(34) Kay, M. I.; Okaya, Y.; Cox, D. E. A Refinement of the Structure of the Room Temperature Phase of Phenanthrene, $C_{14}H_{10}$, from X-ray

and Neutron Diffracrtion Data. *Acta Crystallogr. B* **1971**, *27*, 26.

(35) Hirshfeld, F. L.; Sandler, S.; Schmidt, G. M. J. The Structure of Overcrowded Aromatic Compounds. Part VI. The Crystal Structure of Benzo[c]phenenthrene and of 1,12-Dimethylbenzo[c]phenanthrene *J. Chem. Soc.* **1963**, 2108.

(36) Mason, R. The Crystallography of Anthracene at 95K and 290K. *Acta Crystallogr.* **1964**, *17*, 547.

(37) Ponomarev, V. I.; Shilov, G. V. Kristallitcheskaya struktura antracena v intervale 300−100 K (in Russian). *Kristallograf.* **1983**, *28*, 674.

(38) Robertson, J. M.; White, J. G. The Crystal Structure of the Monoclinic Modification of 1:2−5:6-Dibenzanthracene. A Quantitative X-ray Investigation. *J. Chem. Soc.* **1956**, 925.

(39) Herbstein, F. H. Crystal and Molecular Structures of Overcrowded Halogenated Compounds. VIII. Two Overcrowded Naphthalenes— Octachloronaphtalene and Tetrabenzonaphthalene (Dibenzo[g,p]chrysene). *Acta Crystallogr. B* **1979**, *35*, 1661.

(40) Ferraris, G.; Jones, D. W.; Yerkess, J. A Neutron-Diffraction Study of the Crystal and Molecular Structure of Triphenylene. *Z. Kristallogr.* **1973**, *138*, 113.

(41) Kai, Y.; Hama, F.; Yasuoka, M.; Kasai, N. Structural Chemistry of Layered Cyclophanes. III. Molecular Structures of [2.2](2,7)-Pyrenophane-1,1′-diene and Pyrene (Redetermined). *Acta Crystallogr. B* **1978**, *34*, 1263.

(42) De, A.; Gosh, R.; Roychowdhury, S.; Roychowdhury, P. Structural Analysis of Picene, $C_{22}H_{14}$. *Acta Crystallogr. C* **1985**, *41*, 907.

(43) Marsh, W.; Dunitz, J. D. Crystal Structure of a Double Helicene, Diphenanthro[3,4-a; 3′,4′-o]picene. *Bull. Soc. Chim. Belg.* **1979**, *88*, 847.

(44) Krygowski, T. M.; Ciesielski, A.; Świrska, B.; Leszczyński, P. Variation of Molecular Geometry and Aromatic Character of Chrysene and Perylene in Their EDA complexes. Refinement of X-ray Crystal and Molecular Structure of Chrysene and Perylene. *Pol. J. Chem.* **1994**, *68*, 2097.

(45) Kohno, Y.; Kohno, M.; Saito, Y.; Inokuchi, H. The Crystal Structure of Tetrabenzo[a,cd,j,lm]perylene. *Acta Crystallogr. B* **1975**, *31*, 2076.

(46) Kuroda, R. J. Crystal and Molecular Structure of [5]Helicene: Crystal Packing Models. *J. Chem. Soc., Perkin Trans 2* **1982**, 789.

(47) de Rango, C.; Tsoucaris, G.; Declercq, J. P.; Germain, G.; Putzeys, J. P. Hexahelicene. *Crystallogr. Struct. Commun.* **1973**, *2*, 189.

(48) Beurskens, P. T.; Beurskens, G.; van der Hark, T. E. M. Heptahelicene. *Crystallogr. Struct. Commun.* **1976**, *5*, 241.

(49) Oonishi, I.; Ohshima, S.; Fujisawa, S.; Aoki, J.; Ohashi, Y.; Krygowski, T. M. Conformation of Condensed Polycyclic Aromatic Hydrocarbons. III. The Crystal and Molecular Structure of Tribenzo[a,h,rst]phenanthra[1,2,10-cde]pentaphene. *J. Mol. Struct.* **1992**, *265*, 283.

(50) Fujisawa, S.; Oonishi, I.; Aoki, J.; Ohashi, Y. Structure of Dibenzo-[def,i]naphto[1,8,7-vwx]pyranthrene. *Acta Crystallogr.* **1986**, *C42*, 1390.

(51) Fujisawa, S.; Oonishi, I.; Aoki, J.; Ohashi, Y.; Sasada, Y. Conformation of Condensed Polycyclic Aromatic Hydrocarbons. I. The Molecular and Crystal Structure of Anthra[2,1,9,8-hijkl]benzo[de]naphtho[2,1,8,7-stuv]pentacene. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3424.

(52) Kerr, K. A.; Ashmore, J. P.; Speakman, J. C. The Crystal and Molecular Structure of Quaterrylene: A Redetermination. *Proc. Roy. Soc. London Ser. A* **1975**, *344*, 199.

(53) Hazell, R. G.; Pawley, G. S. The Crystal and Molecular Structure of Ovalene: Some Three-Dimentional Refinements. *Z. Kristallogr.* **1973**, *137*, 159.

(54) Izuoka, A.; Wakui, K.; Fukuda, T.; Sato, N.; Sugawara, T. Refined Molecular Structure of Tetrabenzo[de,hi,op,st]pentacene. *Acta Crystallogr. C* **1992**, *48*, 900.

(55) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.