Pergamon

Tetrahedron 54 (1998) 14919–14924

TETRAHEDRON

Separation of the Energetic and Geometric Contribution to Aromaticity. Part X. The Case of Benzene Rings in Fused Polycyclic Benzenoid Hydrocarbons.

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Received 13 July 1998; revised 25 September 1998; accepted 8 October 1998

Abstract Eight aromaticity indices were estimated by the application of the bond lengths of 18 benzene rings taken from 10 benzenoid hydrocarbons (benzene, naphthalene, anthracene, tetracene, phenanthrene, chrysene, triphenylene, pyrene, perylene and coronene) computed by *ab initio* at RHF 6-31G** level of theory. The following indices were computed: three energetic indices (BE, EN and Hartree Fock energy for a constrained bond lengths in the ring), two geometric indices (Bird's I_6 and GEO) two magnetic indices (Schleyer's NICS for benzene rings in the benzenoid hydrocarbons and another one computed for isolated rings with bond lengths taken from the rings of benzenoid hydrocarbons) and one which is a combination of geometric and energetic indices - HOMA. The application of correlation and factor analyses to the above data matrix (8 indices for 18 rings) led to the conclusion that two orthogonal factors must be used to explain 96.4% of the total variance. The first factor which describes 66.8% is composed mostly of energetic indices (HF, EN and BE), HOMA (which contains both energetic and geometric contributions) and NICS. The second factor describes 29.8% and is built up of geometric indices (GEO, I_6 and BAC). The best correlation coefficient is found for a regression between HF and HOMA values (r-= 0.98). This supports the high utility of the HOMA model in describing aromaticity. NICS correlates well with energetic indices including HF and HOMA and it supports Schleyer's concept of the great importance of magnetic indices in describing aromaticity. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

Benzene is considered as a typically aromatic compound[1] yet when the benzene ring is fused to other rings in benzenoid systems its aromaticity depends strongly on the topological environment.[2-4] This fact may explain the successful application of various graph-topological methods to these kinds of systems leading to a good description of energetic properties and variation of their aromatic character.[5-7] Since a great variation in the geometry of the rings exists in benzenoid hydrocarbons, they represent an excellent, homogeneous sample for studies of aromaticity.

The aim of this report is to analyse to what extent various aromaticity indices (energetic, geometric and magnetic) may be useful in determination of the local aromatic character of benzene rings in benzenoid hydrocarbons. We also intend to test Katritzky's hypothesis[8] on the multidimensional character of the phenomenon called aromaticity.

PII: S0040-4020(98)00934-X

Results and Discussion

The molecular geometry[9] of 18 benzene rings of the following 10 benzenoid hydrocarbons: benzene, naphthalene, anthracene, tetracene, phenanthrene, pyrene, perylene, chrysene, coronene and triphenylene was applied for the computation of various indices of aromaticity. These included HOMA[10] and its components EN and GEO,[11] Bird's I_6,[12] BAC,[13] BE[2] and Schleyer's NICS.[4] The last one was calculated in two different ways: (i) for the rings embedded in the benzenoid hydrocarbons (NICS)[9] and (ii) for the rings for which the molecular geometry was taken from the above systems but HF/6-31G** calculations were carried out[14] for a benzene ring of that geometry (C-C bond lengths constrained, other geometry parameters optimised). The latter procedure was also applied for the computation of the Hartree-Fock energy (denoted HF) and NICS values (denoted NICSB) of benzene rings of such geometry.

Table 1 contains all the data mentioned above, whereas Table 2 shows the results of the total correlation analysis carried out for all these indices of aromaticity.

Table 1. Indices of aromaticity; BE in kcal/mol; NICS, NICSB in ppm, HF in units of Hartree. (e) and (i) denote external and internal rings, respectively.

Compound	HOMA	EN	GEO	BAC	I_6	BE	NICS	NICSB	HF
benzene	1.00	-0.001	0.000	1.000	100.0	735.4	-11.5	-9.66	-230.713860
naphthalene	0.776	0.022	0.202	0.577	75.9	718.6	-11.4	-9.46	-230.710244
anthracene(e)	0.516	0.065	0.420	0.395	64.8	709.4	-9.6	-9.26	-230.705944
anthracene(i)	0.882	0.044	0.074	0.751	85.8	711.5	-14.3	-9.63	-230.711055
phenanthrene (e)	0.901	0.007	0.092	0.727	83.9	724.0	-11.7	-9.58	-230.712113
phenanthrene (i)	0.414	0.183	0.403	0.406	65.0	692.2	-7.4	-9.23	-230.703909
pyrene (e)	0.952	0.014	0.034	0.896	90.4	720.4	-14.5	-9.65	-230.712566
pyrene (i)	0.475	0.179	0.346	0.439	67.2	692.4	-5.6	-9.32	-230.704267
chrysene (e)	0.858	0.010	0.131	0.665	80.7	722.7	-11.5	-9.53	-230.711519
chrysene (i)	0.557	0.119	0.324	0.463	69.0	699.8	-8.7	-9.30	-230.706497
triphenylene (e)	0.929	0.003	0.068	0.775	86.2	727.4	-10.8	-9.60	-230.712576
triphenylene (i)	0.069	0.606	0.325	0.398	69.2	658.4	-3.0	-9.14	-230.697531
tetracene (e)	0.321	0.108	0.571	0.304	58.7	703.1	-6.7	-9.16	-230.702521
tetracene (i)	0.770	0.072	0.158	0.626	78.9	706.2	-13.1	-9.54	-230.709180
perylene (e)	0.790	0.029	0.180	0.629	77.3	716.0	-9.4	-9.50	-230.710079
perylene (i)	-0.111	0.938	0.173	0.619	77.7	640.1	6.8	-9.53	-230.689518
coronene (e)	0.765	0.065	0.170	0.605	77.6	707.7	-12.1	-9.47	-230.709664
coronene (i)	0.628	0.372	0.000	1.000	100.0	672.0	-5.4	-9.61	-230.704503

The indices presented above may be classified into three groups:

(i) the ones describing only a degree of bond length alternation like GEO, I_6 and BAC; they are usually denoted as geometric indices of aromaticity.

(ii) those which are directly related to energy, like EN, BE and, of course, HF, which can be attributed to so-called energetic indices of aromaticity.

(iii) magnetic indices, NICS and NICSB. By definition[4] NICS is a negative value of the absolute magnetic shielding computed[14] at ring centres.

HOMA, which takes into account two kinds of deformation[11] which lead to a dearomatization of the ring, *i.e.* bond length alternation (the GEO term) and bond elongation (the EN term), is beyond this classification.

Table 2. Correlation coefficients and significant levels of the correlations between all the indices from Table 1.

	HOMA	EN	GEO	BAC	I_6	BE	NICS	NICSB
HOMA	1.0000							
	0.0000							
EN	-0.8589	1.0000						
	0.0000	0.0000						
GEO	-0.6126	0.1213	1.0000					
	0.0069	0.6315	0.0000					
BAC	0.6171	-0.1623	-0.9455	1.0000				
	0.0064	0.5199	0.0000	0.0000				
I_6	0.5879	-0.1202	-0.9538	0.9933	1.0000			
	0.0103	0.6347	0.0000	0.0000	0.0000			
BE	0.8954	-0.9510	-0.2676	0.2979	0.2569	1.0000		
	0.0000	0.0000	0.2830	0.2298	0.3035	0.0000		
NICS	-0.8955	0.9260	0.3066	-0.3001	-0.2766	-0.8805	1.0000	
	0.0000	0.0000	0.2159	0.2263	0.2665	0.0000	0.0000	
NICSB	-0.6700	0.2292	0.9447	-0.9178	-0.8982	-0.3802	0.3570	1.0000
	0.0024	0.3602	0.0000	0.0000	0.0000	0.1196	0.1458	0.0000
HF	-0.9803	0.9295	0.4654	-0.4722	-0.4447	-0.9439	0.9422	0.5149
	0.0000	0.0000	0.0516	0.0478	0.0644	0.0000	0.0000	0.0288

The results shown in Table 2 indicate that there are good intrinsic correlations for indices within each of the groups (i) and (ii). The absolute value of the correlation coefficient for any pair within a given group is always greater than 0.92. On the other hand, these two kinds of indices are not correlated (if pairs are built up of indices belonging to two different groups). The absolute values of the correlation coefficients for these kinds of pairs are always less than 0.48.

An important conclusion is that **dearomatization due to the changes in molecular geometry expressed *via* bond length alternation is not correlated with the dearomatization which results from the mean bond length extension**. Moreover, the above results strongly support the validity of the approximate indices of aromaticity like EN (based only on mean bond lengths), or BE (based on a very simple model relating exponentially bond energy to the bond length),[2] since both of them correlate very well with the more realistic estimation of energy of the rings computed *via* RHF procedure for constrained C-C bond length geometry.

The magnetic index NICS, computed for the rings embedded in the benzenoid moiety, correlates well with HF, r = 0.94 and with HOMA, r = -0.90. HOMA which is composed of two components has the best correlation coefficient of all indices with HF values with r = -0.98. Scatter plots in Fig 1 present correlations of

NICS, HOMA, EN and GEO, showing clearly that three first indices correlate well with HF whereas the GEO term does not.

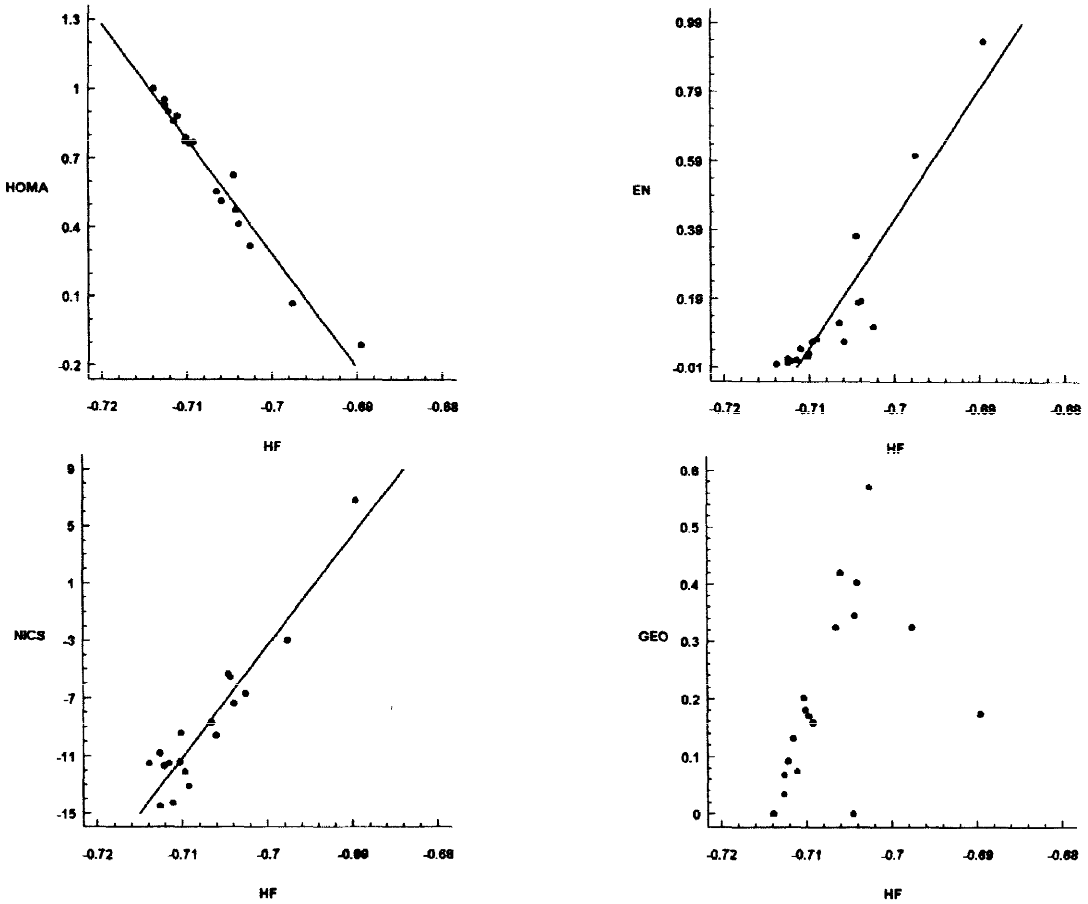

Fig 1. Scatter plots of HOMA, EN, NICS and GEO *vs* HF.

It should be noted that there is a complete lack of correlation between NICS and NICSB. This results from quite different shapes of the π-wave function for the two situations presented above. In the first case, NICS monitors the wave function of a given ring as a part of a function describing the whole molecule. It contains much more information than in the second case of NICSB, where the function is limited to the ring in question, even if the ring has the same C-C bond lengths. It may be concluded that NICS should be computed for the whole molecule if we wish to get reliable information even for a small fragment of this system. A great sensitivity of NICS values to the molecular environment may recall a well known fact that NMR chemical shifts are very sensitive to environmental effects (both, intra- and inter-molecular), being an extraordinary tool for structural studies. Taking into account all these facts, the differences in values of NICS and NICSB are understandable. Moreover this may be a good indication for using NICS to study subtle structural effects in describing aromaticity, in analogy to NMR spectroscopy applications for structural studies.

The application of factor analysis[15] to the data of Table 1 shows that two factors describe 96.4% of the total variance (the other being insignificant). The first one, which describes 66.8%, may be identified with HF, NICS, HOMA and energetic indices like EN and BE. Geometric indices contribute to a less important factor (29.6%), and hence the bond length alternation as a determinant of non-aromaticity should not be overestimated.

The results obtained here resemble those obtained for benzene rings in meta- and para-cyclophanes[16] where the variation in bond lengths in the ring was much smaller. The difference is also that in this report the variation in aromatic character is analysed over the full scale of HOMA from 0.07 for the central ring in triphenylene to 0.98 for benzene itself and some cases of peripheral rings in benzenoid hydrocarbons, compared to the range 0.92 - 1.00 in the case of cyclophane derivatives.

The most important conclusion of this report is that **even in such a homogeneous sample as that of benzene rings in benzenoid hydrocarbons, two orthogonal factors are necessary to describe about 96% of the total variance**. These two factors are: (i) the energetic (~67%) and (ii) geometric ~30%) one. Additionally, it can be concluded that **the magnetic index, NICS, does not form a separate factor, but it contributes to the first factor which correlates best with the energetic indices and HOMA. Paradoxically, these results may be used as a support for Schleyer's concept[17,18] that magnetic criteria are of great importance for determination of aromaticity.**

Acknowledgements

Both authors acknowledge the Interdisciplinary Centre for Mathematical and Computational Modelling (Warsaw University) for computational facilities. Financial support by KBN 3T09A 019 13 grant is gratefully acknowledged. We are also grateful to Dr H Elżanowska for careful reading of the manuscript and providing usefull comments.

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