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Separation of the Energetic and Geometric Contributions to Aromaticity. Part VIII. Changes in Aromaticity and the Evidence for the Multi-Dimensionality of the Aromatic Character of Benzene Rings in Para- and Meta-Cyclophanes*

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Abstract: Seven quantitative measures of aromaticity: I_6, HOMA, EN, GEO, HOSE, BE and BAC, for benzene itself and 39 benzene rings in 26 meta- and para-cyclophane derivatives are used for the study of the aromaticity of the benzene ring in these systems. The indices calculated from molecular geometry and supplemented by RHF/6-31G* energy calculations for each ring geometry are the subject of correlation and factor analyses. As a result evidence of a formal two-dimensional character of aromaticity is clearly shown. The first factor describing 49.8% of the total variance is mostly contributed by energetic indices (EN, BE, HOSE and RHF calculated energy, and to a lesser extent HOMA), the next factor describing 44.8% of the total variance depends mostly on geometric indices (I_6, GEO, BAC and partly HOMA). The HOMA index being composed of two contributions, energetic and geometric, correlates very well with RHF energies, which also take into account all conributions due to the deformations of the ring geometry. Deformations of benzene rings in cyclophanes due to substitution decrease aromaticity only slightly.

INTRODUCTION

Cyclophanes belong to a group of π-electron systems in which benzene rings are somewhat bent and in almost parallel (averaged in the meaning of the best least square plane of the ring) planes at a close distance of about 2.5-3.0 Å[1] and hence giving an opportunity of special interactions between the rings leading to some changes in their behaviour.[2] These interactions are not too strong and are relatively homogeneous in nature, hence the systems under study may be used to examine the controversial problem of the dimensionality of aromaticity. The problem arose after the famous papers by Katritzky et al.,[3] which were followed by subsequent reports.[4-6] A general conclusion was that aromaticity is a multidimensional phenomenon, with two or three independent (orthogonal) factors contributing to the term. They could be roughly identified with the criteria of aromaticity established in the sixties[7] as:

(i) energetic criterion based on an increase of chemical stability quantified by the resonance energy or related terms,

(ii) geometric criterion based on observation of averaging of bond lengths in aromatic systems, and

(iii) magnetic criteria related to ^{1}H-NMR chemical shifts and magnitude of anisotropy of magnetic susceptibility.

* Dedicated to Professor Alan Roy Katritzky on the occasion of his 70th.birthday.

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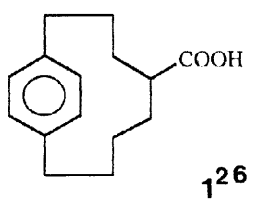
The philosophy of multidimensionality was opposed by a statement of Schleyer,[8] who proposed a definition[8,9] that "compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic delocalization may also result in bond length equalisation, abnormal chemical shift and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilisation". This statement seems to over estimate the magnetic criterion relative to energetic and geometric ones, which are closer to chemical tradition and facility of measurement, respectively. Recently Schleyer has proposed[10] an effective parameter which measures "magnetic aromaticity" called NICS (abbreviation from nucleus independent chemical shift). This parameter has proved to be very useful for describing the aromaticity of various π-electron systems,[10] including heteroaromatics[11] and porphyrins,[12] indicating in the latter case a reasonable agreement with the geometry-based index HOMA.[13,14]

The purpose of this paper is to discuss the aromatic character of benzene rings in cyclophanes together with a study of dimensionality in respect of the term aromaticity.

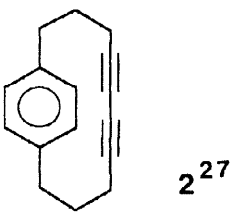
Aromatic Character of the Ring in Cyclophanes

When the bond lengths of the benzene ring in the title compounds are transformed into the aromaticity indices: HOMA,[13] EN,[14] GEO,[14] I_6,[15] BAC,[6,16] BE,[16] HOSE[17] it transpires that the benzene rings involved in the cyclophane moieties maintain their aromatic character with the mean values of aromaticity indices near to those of benzene itself. Chart 1 presents the relevant data.

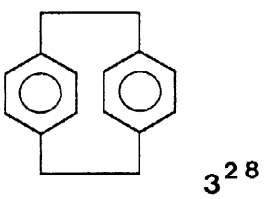
Chart 1. Aromaticity indices HOMA, EN, GEO, BAC, I_6, BE, HOSE (abbreviated H, E, G, B, I6, BE, HS, respectively) for meta- and para-cyclophanes. Letters in parenthesis label individual rings.



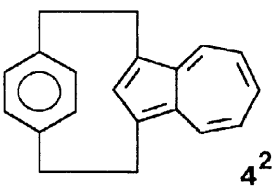
1[26]
H=0.989
E=0.001
G=0.010
B=0.910
I6=94.7
BE=728.9
HS=49.52



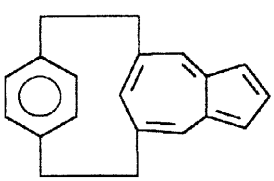
2[27]
H=1.005
E=-0.009
G=0.004
B=0.949
I6=96.7
BE=742.1
HS=54.02



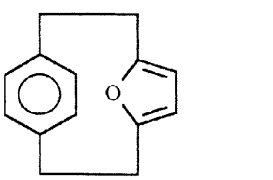
3[28]
H=1.003
E=-0.003
G=0.000
B=0.986
I6=99.2
BE=737.7
HS=48.02



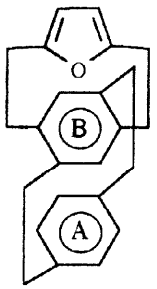
4[29]
H=0.961
E=0.021
G=0.018
B=0.878
I6=93.02
BE=717.5
HS=46.07



5[30]
H=0.959
E=0.014
G=0.028
B=0.852
I6=91.31
BE=720.3
HS=47.04



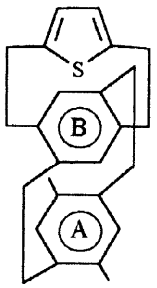
6[31]
H=0.963
E=-0.002
G=0.039
B=0.824
I6=89.70
BE=737.1
HS=52.61



7^{32}

H(A)=0.995
E(A)=0.000
G(A)=0.005
B(A)=0.935
I6(A)=96.25
BE(A)=733.5
HS(A)=50.98

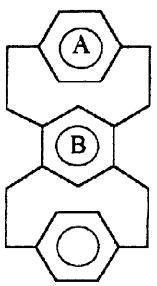
H(B)=0.971
E(B)=0.009
G(B)=0.019
B(B)=0.874
I6(B)=92.73
BE(B)=722.4
HS(B)=47.50



8^{32}

H(A)=0.981
E(A)=-0.002
G(A)=0.021
B(A)=0.881
I6(A)=92.53
BE(A)=737.0
HS(A)=51.96

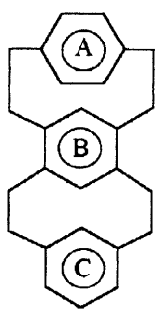
H(B)=0.937
E(B)=0.006
G(B)=0.057
B(B)=0.787
I6(B)=87.56
BE(B)=724.9
HS(B)=48.85



9^{33}

H(A)=0.988
E(A)=0.010
G(A)=0.002
B(A)=0.955
I6(A)=97.42
BE(A)=722.0
HS(A)=47.20

H(B)=0.978
E(B)=0.017
G(B)=0.005
B(B)=0.933
I6(B)=96.19
BE(B)=719.1
HS(B)=46.34

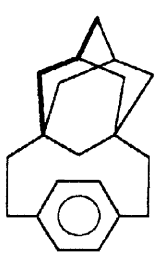


10^{33}

H(A)=0.978
E(A)=0.004
G(A)=0.019
B(A)=0.890
I6(A)=92.89
BE(A)=726.0
HS(A)=48.83

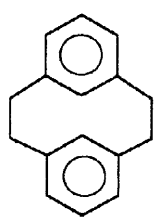
H(B)=0.948
E(B)=0.046
G(B)=0.006
B(B)=0.926
I6(B)=95.79
BE(B)=710.5
HS(B)=43.71

H(C)=0.989
E(C)=0.007
G(C)=0.004
B(C)=0.942
I6(C)=96.77
BE(C)=723.7
HS(C)=47.55



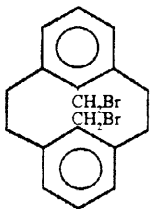
11^{34}

H=0.991
E=0.000
G=0.0086
B=0.915
I6=95.18
BE=731.6
HS=50.39



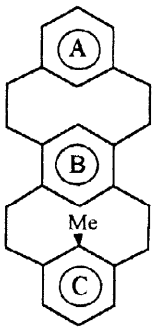
12^{35}

H=0.981
E=0.0179
G=0.0011
B=0.982
I6=98.28
BE=718.5
HS=46.05



13[36]

H=0.954
E=0.003
G=0.043
B=0.863
I6=89.35
BE=726.7
HS=49.29

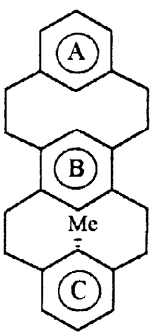


14[37]

H(A)=0.988
E(A)=0.002
G(A)=0.010
B(A)=0.925
I6(A)=94.73
BE(A)=727.8
HS(A)=49.08

H(B)=0.962
E(B)=0.031
G(B)=0.007
B(B)=0.928
I6(B)=95.63
BE(B)=714.2
HS(B)=44.98

H(C)=0.958
E(C)=0.009
G(C)=0.033
B(C)=0.897
I6(C)=90.57
BE(C)=722.5
HS(C)=47.86

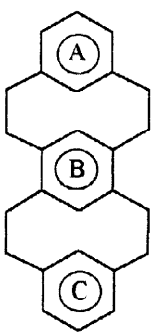


15[38]

H(A)=0.992
E(A)=-0.006
G(A)=0.014
B(A)=0.912
I6(A)=93.79
BE(A)=740.5
HS(A)=53.37

H(B)=0.972
E(B)=0.026
G(B)=0.002
B(B)=0.960
I6(B)=97.43
BE(B)=715.8
HS(B)=45.39

H(C)=0.949
E(C)=0.000
G(C)=0.051
B(C)=0.854
I6(C)=88.11
BE(C)=732.2
HS(C)=51.02

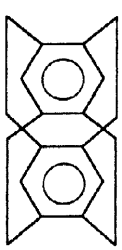


16[39]

H(A)=0.994
E(A)=0.001
G(A)=0.005
B(A)=0.943
I6(A)=96.29
BE(A)=729.1
HS(A)=49.46

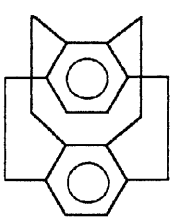
H(B)=0.962
E(B)=0.036
G(B)=0.002
B(B)=0.958
I6(B)=97.54
BE(B)=712.9
HS(B)=44.57

H(C)=0.992
E(C)=0.002
G(C)=0.006
B(C)=0.943
I6(C)=95.96
BE(C)=727.5
HS(C)=48.96



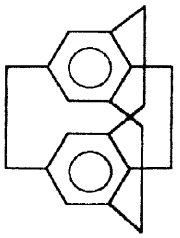
17[40]

H=0.944
E=0.041
G=0.015
B=0.889
I6=93.71
BE=711.6
HS=45.26



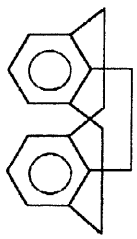
18[41]

H=0.959
E=0.000
G=0.041
B=0.876
I6=89.37
BE=731.1
HS=50.54



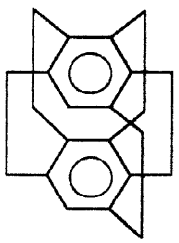
19[41]

H=0.965
E=0.006
G=0.029
B=0.890
I6=91.02
BE=724.7
HS=48.26



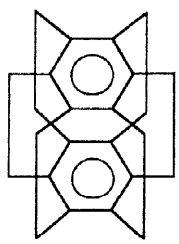
20[42]

H=0.969
E=0.000
G=0.031
B=0.906
I6=90.81
BE=733.5
HS=51.45



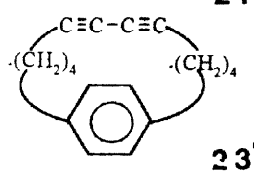
21[42]

H=0.956
E=0.029
G=0.015
B=0.926
I6=93.59
BE=714.8
HS=45.34



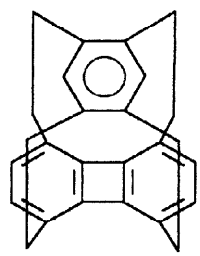
22[42]

H=0.916
E=0.084
G=0.000
B=1.000
I6=100.00
BE=703.0
HS=42.04



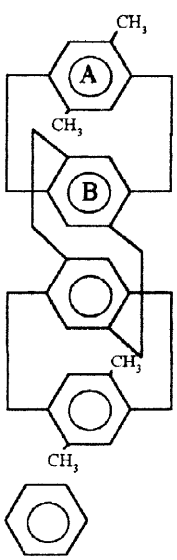
23[43]

H=0.976
E=-0.010
G=0.035
B=0.828
I6=90.31
BE=742.9
HS=54.14



24[44]

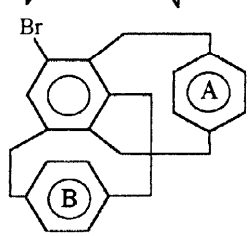
H=0.981
E=0.008
G=0.011
B=0.905
I6=94.53
BE=723.2
HS=48.94



25[45]

H(A)=0.985
E(A)=0.001
G(A)=0.014
B(A)=0.896
I6(A)=93.77
BE(A)=729.8
HS(A)=49.45

H(B)=0.994
E(B)=0.000
G(B)=0.006
B(B)=0.954
I6(B)=95.97
BE(B)=732.7
HS(B)=50.71



26[46]

H(A)=0.924
E(A)=0.018
G(A)=0.059
B(A)=0.779
I6(A)=87.20
BE(A)=718.9
HS(A)=47.33

H(B)=0.993
E(B)=0.007
G(B)=0.000
B(B)=0.993
I6(B)=99.61
BE(B)=723.4
HS(B)=47.57

27[47]

H=0.979
E=0.021
G=0.000
B=1.000
I6=100.00
BE=717.4
HS=45.80

The main conclusion to be drawn from the data in the chart is that benzene rings embedded in cyclophane moieties do not loose aromatic character more than any other para- or meta-disubstituted and 1,2,4,5-tetrasubstituted benzene derivatives.[18]

If the mean values of aromaticity indices for the outer and inner rings are compared, then the values for the outer ones are always greater than those for the inner rings but this may be merely an effect of the tetra substitution of the inner rings (four links to carbons of the outer rings) compared to only two links for the outer rings. Analysis of substituted benzene rings[18] shows that for the HOMA index these values are alike: para

disubstituted benzenes have HOMA = 0.99 and 1,2,4,5-tetrasubstituted ones have HOMA = 0.97. Thus the observed result is in line with that found for individual rings of similarly substituted benzenes. Additionally the energetic indices (EN, BE and HOSE) exhibit a significant difference for these two kinds of rings. This may be due to the different possibilities of thermal motion for these two sorts of rings: the doubly-linked rings (the outer ones) are allowed to librate, whereas the the tetra-linked outer inner ones are not. This difference contributes to the greater changes in bond length for the doubly-linked rings.[19]

Correlation Analysis

Apart from calculating indices of aromaticity we have used the experimental geometry of the benzene rings in cyclophanes to calculate energy within *ab initio* at RHF/6-31G* level[20] assuming constrained CC bond lengths and with all other geometry parameters optimised, These data labelled HF (abbreviation from Hartree Fock energy) were then correlated with all of the other aromaticity indices. Table 1 shows the resulting correlation coefficients with significance levels in a lower row.

Table 1. Correlation Coefficients and the Levels of Significance (below) for the Pairs of Aromaticity Indices

	HOMA	EN	GEO	BAC	I_6	BE	HOSE
EN	-0.6400						
	0.0000						
GEO	-0.5660	-0.2713					
	0.0001	0.0904					
BAC	0.4670	0.2964	-0.9027				
	0.0024	0.0633	0.0000				
I_6	0.4749	0.3403	-0.9601	0.9423			
	0.0020	0.0317	0.0000	0.0000			
BE	0.5872	-0.9004	0.2304	-0.2412	-0.2815		
	0.0001	0.0000	0.1527	0.1338	0.0785		
HOSE	0.4700	-0.8692	0.3438	-0.3665	-0.4098	0.9619	
	0.0022	0.0000	0.0298	0.0200	0.0086	0.0000	
HF	-0.9770	0.7466	0.4228	-0.3286	-0.3312	-0.6660	-0.5546
	0.0000	0.0000	0.0066	0.0384	0.0368	0.0000	0.0002

It is immediately clear that there are some obvious intercorrelations between the indices: all indices called "geometric" like GEO, BAC, I_6 are mutually well correlated. The best correlations are observed between I_6 and GEO(-0.960) and then between I_6 and BAC (0.942). This is clearly because I_6, GEO and BAC are typical geometric indices measuring solely the extent of bond alternation. Interestingly, there is a weak correlation (between 0.47 and 0.57) of these indices with HOMA, which can be attributed to the fact that this index is composed[14] of both geometric and energetic terms. The other group of mutually correlated indices are EN, BE and HOSE. The best correlations are between HOSE and BE (0.962) and BE and EN (-0.900). It is worth stressing that HF correlates very well with HOMA (-0.977), moderately well with energetic indices (0.55 - 0.75), and markedly worse with geometric indices (0.33 - 0.42). Figure 1 presents the scatter plots of HOMA and I_6 with HF.

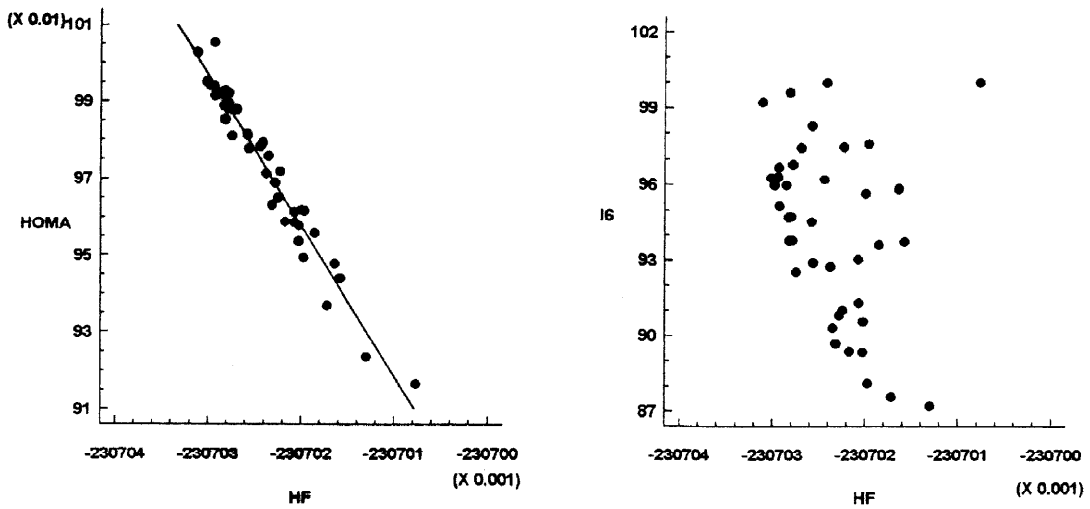


Fig. 1 Scatterplots of HOMA and I_6 *vs* HF

These results may be interpreted as follows. HOMA, which is composed of two terms, takes into account both the alternation effect *(via* GEO term) and the energetic effect due to changes of the mean bond length (*via* EN term). From the statistical point of view[21] both of these terms corelate with HF: the first one at significance level $\alpha<0.01$ and the second one at $\alpha<0.0001$. Thus both terms contribute significantly to the description of the variance of HF. Both kinds of deformation, i.e. expansion or compression of the ring measured *via* the changes in mean CC bond lengths in the benzene ring and the bond length alternation cost energy. Thus both of them are energetic in nature.[22] However, the GEO term is called "geometric" because it arises from a traditional measure of the "geometric" criterion of aromaticity, i.e. the alternation of bond lengths. The other contribution to the overall aromaticity is estimated within the HOMA index by the EN term. This term solely measures changes of energy due to the expansion or compression of the bond length and has never been taken into account in the definition of geometry based aromaticity indices. Therefor HF which measures both effects corrlates very well with HOMA, and significantly with its component EN and GEO terms. HF also correlates significantly with other energetic indices of aromaticity, but not with geometric indices. This is not surprising since bond length alternation represents aromatic character only in a partial way.[23]

Factor Analysis

The intercorrelations presented above are even better shown by use of factor analysis.[24] Table 2 presents the results of application of 7 indices of aromaticity and HF for the 40 benzene rings in question. The results are very indicative: two factors describe 94.6 % of the total variance. The first factor explaining 49.8 % of the total variance may be identified with"energetic" indices: EN, BE, HOSE, HF, and the mixed one HOMA. The absolute values of loadings for the energetic indices are greater than 0.85, whereas the other indices (the "geometric" ones) contribute only marginally to this factor. In contrast to this, the second factor describing 44.8 % of the total variance is related almost entirely to the "geometric" indices, with absolute values of loadings greater than 0.95. HOMA and HF are also present in the second factor with loadings of 0.60 and 0.47, respectively. The presence of these parameters in both factors means that both, HF and HOMA, take into account aromaticity in a more

holistic way. In conclusion, the multidimensionality of aromaticity is once again exhibited and well supported. It should be stressed however, that the separation of HOMA (and aromaticity) into GEO and EN terms is somewhat formal since both contributions, the "geometric" and "energetic" terms, are associated with changes of the total electronic energy of the system in question.

Table 2. Loadings of Two Main Factors.

Variable/ Factor (% of the total variance)	1 (49.8%)	2 (44.8%)
HOMA	0.78310	0.60387
EN	-0.95433	0.20984
GEO	0.04292	-0.98152
BAC	-0.09769	0.95003
I_6	-0.12603	0.97603
BE	0.94376	-0.19586
HOSE	0.89502	-0.32947
HF	-0.85434	-0.47138

Conclusions

Benzene rings in cyclophanes represent a rather homogeneous group of rings of high aromaticity, hence they seem to be adequate to analyse problems related to the definition and dimensionality of aromaticity.

All aromaticity indices applied in this paper are based on experimental bond lengths, and hence they could be suspected of being mutually dependent as they are based on the same set of data. The results of correlation and factor analyses strongly oppose this thinking. Two orthogonal factors contribute to an explanation of the total variance.

This may thus be accepted as evidence that the **aromaticity of benzene rings perturbed in cyclophanes as shown in Chart 1 is a formally two-dimensional phenomenon.**

Hartree Fock energies of benzene rings calculated for CC constrained geometry correlate very well with the HOMA values. **This index is known to be composed of two terms depending on the bond length alternation and changes of the mean bond length from the optimal value and therefore correlates very well with HF's. Since the HF energy may be related to the resonance energy, one of the oldest and well grounded indices of aromaticity,[25] the above statement may approve the high qualification of HOMA as an index describing the overall aromaticity of π-electron systems.**

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