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Two Sources of the Decrease of Aromaticity: Bond Length Alternation and Bond Elongation. Part II. An Analysis Based on Geometry of the Singlet and Triplet States of 4nπ Annulenes: C_4H_4, $C_5H_5^+$, $C_6H_6^{2+}$, $C_7H_7^-$, C_8H_8, $C_9H_9^{+*}$

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Abstract. Triplet states of 4nπ-electron annulenes exhibit partly aromatic character with an increase of aromaticity as the size of the ring increases. Small effects of dearomatisation are due to bond elongation. Singlet states are antiaromatic, their dearomatisation is mostly due to the bond length alternation. Correlation analysis applied to basic indices of aromaticity ($\delta(^1H)$, NICS, HOMA and χ) practically shows the lack of any correlation in sub-groups consisting of triplets or singlets.

Key words: Aromaticity, Annulenes, Excited States.

Introduction

Aromaticity of molecules in their excited states has long been subject of great interest.[1-10] Almost thirty years ago Baird[1] suggested that 4nπ electron annulenes in the triplet state are aromatic rather than antiaromatic. This view was later supported by many studies.[2-9] Very recently high level *ab initio* calculated[9] magnetic properties for the triplet and singlet states of 4nπ annulenes have fully supported Baird's idea: proton chemical shifts for triplets of 4nπ annulenes are like that for benzene (7.8 ppm) whereas those for singlets resemble rather olefinic systems. Magnetic susceptibilities, diamagnetic susceptibility exaltations and nucleus independent chemical shifts (NICS)[11] have the values typical of aromatic compounds - NICS values are negative for triplets and positive for singlets, magnetic susceptibilities are more negative for triplets than for singlets. Aromatic stabilisation energies computed for triplet states of C_4H_4 and $C_5H_5^+$ support their higher stability than for singlets.[9] Bond lengths for triplets have no alternation, whereas a strong alternation is observed for singlets. However, these results are not conclusive, since the equality of bond lengths is not a good criterion of aromaticity: five membered rings in fullerene C_{60} are not aromatic[10,12,13] in spite of the lack of any bond alternation. The same is true for radialene.[14]

The aim of this report is to show how far a decrease in the aromatic character depends on the bond elongation as compared with a decrease due to the bond alternation. Molecular geometry allows us to analyse

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this problem quantitatively by use of the HOMA-index[15] in which the components describing a decrease in aromaticity due to the bond elongation (EN-term) and due to the bond alternation (GEO-term) are computed directly from bond length:[16]

$$HOMA = 1 - \alpha(R_{opt} - R_{av})^2 - {}^{\alpha}/_{n} \Sigma (R_{av} - R_i)^2 = 1 - EN - GEO \qquad (1)$$

where n is the number of bonds taken into the summation and α is an empirical constant fixed to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems (with bond lengths as in 1,3-butadiene), [17] and 1 for the system with all bonds equal to the optimal value R_{opt} which is equal to 1.388 Å for CC bonds. R_{av} stands for the average bond length, while the individual bond lengths are labeled by R_i.

Recently this kind of approach has been successfully applied to show quantitatively the reasons for the decrease of aromaticity of the central rings in triphenylene- and phenanthrene-like systems[14] where the nature of the low aromatic character could till now be only qualitatively described by the Clar clasification:[18] as „empty" rings or rings with localised double bonds.

Results and Discussion

The molecular geometry of 4nπ-annulenes for singlet- and triplet states[9] was applied for computing HOMA, EN and GEO terms of equation (1). Table I presents these data compared with other aromaticity characteristics.

Table I. Aromaticity characteristics of 4nπ-electron annulenes.
S and T stand for singlet and triplet states, respectively.

compound	Point group	$\delta(^1H)$[9]	NICS[9]	Magnetic susceptibility (χ)[9]	HOMA	EN	GEO
C_4H_4	$S(D_{2h})$	5.9	27.6	7.7	-3.99	1.16	3.84
	$T(D_{4h})$	7.4	-5.3	-22.8	0.30	0.70	0.00
$C_5H_5^+$	$S(C_{2v})$	5.2	49.2	4.8	-1.34	0.51	1.83
	$T(D_{5h})$	8.0	-4.5	-28.4	0.67	0.33	0.00
$C_6H_6^{2+}$	$S(C_s)$	7.0	11.0	-13.7	0.29	0.39	0.32
	$T(D_{3d})$	8.5	-1.5	-28.2	0.61	0.39	0.00
$C_7H_7^-$	$S(C_2)$	3.1	42.9	24.7	0.18	0.18	0.64
	$T(D_{7h})$	7.7	-11.9	-64.5	0.83	0.17	0.00
C_8H_8	$S(D_{2d})$	6.0	3.0	-46.2	-0.21	0.08	1.12
	$T(D_{8h})$	8.1	-12.4	-81.6	0.94	0.06	0.00
$C_9H_9^+$	$S(C_s)$	1.0	9.1		0.30	0.13	0.57
	$T(C_s)$	8.6	-9.7		0.91	0.08	0.01
C_6H_6		7.8	-9.7	-51.3	0.99	0.01	0.00

It is immediately apparent that the analysis by use of the HOMA-model provides us with additional information on the nature of dearomatisation in the singlet and triplet states of 4nπ-annulenes. It is in line with the classification for antiaromatic (singlets) and aromatic (triplets). However, the dearomatisation of triplets is observed and shown to be due to the bond elongation - the EN term decreases from 0.70 for C_4H_4 to 0.06 for C_8H_8. Evidently as the size of the ring increases, this stimulates a lesser dearomatisation, which, except in the case of $C_9H_9^+$, is due only to the bond elongation. In that case a small component of the term due to the bond alternation appears (GEO=0.01). Contrary to that picture, singlets are mostly dearomatised due to the strong bond alternation (the GEO term), which expressed as a percentage contribution is about 80% (except 44.6% for $C_6H_6^{2+}$).

The whole sample of singlets and triplets of 4nπ-electron annulenes is a convenient family to study the dimensionality of aromaticity. Topologically it is a uniform group, and the differences are only in the electronic structure which responds to geometry and other properties of these systems. This group may be further divided into two sub-groups - triplets and singlets, which differ significantly in electronic structure. Moreover, it should be emphasised here that aromaticity is usually defined for ground states of molecules,[7,19] and the further discussion should be considered as an approximate approach to the problem - in analogy to the ground states.

Therefore in our analysis we have taken into account four sub-samples: (i) the lowest energy states (singlets or triplets), (ii) excited states (singlets or triplets), (iii) triplet states, and (iv) singlet states. For all sub-samples we have applied factor and correlation analyses taking into account the values of HOMA, NICS, $\delta(^1H)$ and χ.

Application of the factor analysis revealed that for all four cases two or three factors are necessary to explain 90.4 - 100% of the total variance. However, the interpretation of these factors after rotating is not clear - probably due to a very low correlation between descriptors and the small size of the sample.

Correlation analysis of these four sub-samples shows that only in a few cases there is a significant correlation between aromaticity indices: for sub-sample (i) only correlation between HOMA and NICS is significant (at $\alpha = 0.01$), correlation coefficient $r = 0.97$. However the distribution of points on the scatter plot shows that correlation is due to one point and a cluster of four others; for sub-sample (ii) only correlation between $\delta(^1H)$ and NICS is significant (at $\alpha = 0.05$), $r = 0.89$; for sub-sample (iii) only correlation between χ and NICS is significant (at $\alpha = 0.05$), $r = 0.92$. Correlation is dominated by two clusters; for sub-sample (iv) there are no significant correlations.

In order to illustrate low intercorrelations between aromaticity indices, Tables II - V present the full output of correlation analysis for (i), (ii) , (iii) and (iv) sub-samples.

Table II. Correlation coefficients (and significance levels) for sub-sample (i) with ground state molecules.

	$\delta(^1H)$	NICS	χ
NICS	-0.7138		
	(0.1757)		
χ	-0.2219	0.8021	
	(0.7199)	(0.1025)	
HOMA	0.7422	-0.9742	-0.7026
	(0.1509)	(0.0050)	(0.1857)

Table III. Correlation coefficients (and significance levels) for sub-sample (ii) with exited state molecules.

	$\delta(^1H)$	NICS	χ
NICS	-0.8887		
	(0.0438)		
χ	-0.8598	0.8485	
	(0.0617)	(0.0692)	
HOMA	0.4652	-0.7916	-0.6119
	(0.4298)	(0.1105)	(0.2727)

Table IV. Correlation coefficients (and significance levels) for sub-sample (iii) with molecules in the triplet state.

	$\delta(^1H)$	NICS	χ
NICS	0.3280		
	(0.5900)		
χ	-0.0630	0.9182	
	(0.9198)	(0.0278)	
HOMA	0.4205	-0.6808	-0.8637
	(0.4809)	(0.2058)	(0.0592)

Table V. Correlation coefficients (and significance levels) for sub-sample (iv) with molecules in the singlet state.

	$\delta(^1H)$	NICS	χ
NICS	-0.6968		
	(0.1910)		
χ	-0.7215	0.8744	
	(0.1689)	(0.0524)	
HOMA	-0.1539	-0.2130	-0.0224
	(0.8049)	(0.7308)	(0.9715)

The following conclusions can be drawn:

(i) Aromaticity indices are defined for molecules in their ground states.[7,19] In these cases some of the molecules have triplet ground state, others singlet. Analysis of the whole sample is therefore not justified.

(ii) All the information for the studied systems was computed at high levels of *ab-initio* technique, but its efficiency is different for uncharged, singly charged and doubly charged systems.

If we take into account the above limitations, the conclusion is that the multidimensionality of the aromatic character of $4n\pi$-electron annulenes is exhibited in these cases in a striking way. Very low correlation

between a few cases of only doubtful statistical value (improper distribution within the sample under study) strongly suggests a multidimensional character of aromaticity or inadequate description of the aromatic character in these kinds of molecular state. The small size of the sample used in this study makes these conclusions even stronger.

A positive conclusion may be that the decrease in aromaticity as compared with the paradigm molecule - benzene in the ground state - is due to two mechanisms: depending on either bond elongation (in triplet states) or bond length alternation (more than 75% of the variation in all singlet states (except $C_6H_6^{2+}$)). These results are fully in line with the concept of multidimensional character of aromaticity introduced by Katritzky et al[20-23] and others.[24-27]

References

1. Baird, N. C., *J. Am. Chem. Soc.* **1972**, 94, 4941-4948.
2. Daugherty, R. C., *J. Am. Chem. Soc.* **1971**, 93, 7187-7207 .
3. Aihara J., *Bull. Chem. Soc. Jpn.*, **1978**, 51, 1788-1792.
4. Frataev, F., Monev, V. and Janoschek, R., *Tetrahedron*, **1982**, 38, 2929-2932.
5. Jug, K. and Malar, E. J. P., *J. Mol. Struct. (THEOCHEM)* **1987**, 153, 221-226.
6. Wan, P. and Shukla, D., *Chem. Rev.* **1993**, 93, 571-582.
7. Minkin, V. I., Glukhovtsev, M. N. and Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, J. Wiley, New York, **1994**.
8. Dietz, F., Vogel, H., Schleither, A., Tyutyulkov, N. and Rabinowitz, M., *Z. Naturforsch.*, **1997**, 52b, 1072 -1076.
9. Gogonea, V., Schleyer, P. v. R., and Schreiner, P. R., *Angew. Chem., Int. Ed. Engl.*, **1998**, 37, 1945-1948.
10. T. M. Krygowski, M. Cyrański, *Advances in Molecular Structure Research* (Hargittai, I., Hargittai, M. Eds), vol. 3, 227-268, JAI Press **1997**.
11. Schleyer, P. v. R., Maerker, C., Dransfield, A., Jiao, H., Hommes, N. v. E., *J. Am. Chem. Soc.*, **1996**, 118, 6317-6318.
12. Prato, M., Suzuki, T., Wudl, F., Lucchini, V. and Maggini, M., *J. Am. Chem. Soc.*, **1993**, 115, 7876-7877.
13. Krygowski, T. M. and Ciesielski, A., *J. Chem. Inf. Comput. Sci.*, **1995**, 35, 1001 - 1003.
14. Cyrański, M. K. and Krygowski, T. M., *Tetrahedron*, **1999**, 55, 6205 - 6210.
15. Krygowski, T. M., *Chem. Inf. Comput. Sci.*, **1993**, 33, 70 -78.
16. Krygowski, T. M. and Cyrański M., *Tetrahedron*, **1996**, 52, 1713-1722.
17. Kveseth, K., Seip, R. and Kohl, D.A., *Acta Chem. Scand.*, **1980**, 34, 31-42.
18. Clar E., *Polycyclic Hydrocarbons*, Academic Press, London, **1964.**
19. Schleyer, P. v R., Jiao, H., *Pure Appl. Chem.*, **1996**, 68, 209-218.
20. Katritzky A. R., Barczyński P., Musumurra, G., Pisano D. and Szafran, M., *J. Am. Chem. Soc.*, **1989**, 111, 7-14.

21. Katritzky, A. R., Feygelman, V., Musumurra, G., Barczyński, P. and Szafran, M., *J. Prakt. Chem.* **1990**, 332, 853-869.
22. Katritzky, A. R., Feygelman, V., Musumurra, G., Barczyński, P. and Szafran, M, *J. Prakt. Chem.* **1990**, 332, 870-884
23. Katritzky, A. R., Barczyński, P., *J.Prakt. Chem.*, **1990**, 332, 885-897.
24. Jug, K. and Koster, A. M., *J. Phys. Org. Chem.*, **1991**, 4, 163-167.
25. Krygowski, T. M., Ciesielski, A., Bird, W.C. and Kotschy A., *J. Chem. Inf. Comput. Sci.* **1995**, 35, 203-210.
26. Cyrański, T. M. Krygowski, *Pol. J. Chem.* **1995**, 69, 1088-1096.
27. Katritzky, A. R., Karelson, M., Sild S., Krygowski, T. M. and Jug, K., *J. Org. Chem.*, **1998**, 63, 5228-5231.