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The $2(N+1)^2$ rule for spherical aromaticity: further validation

Received: 24 January 2001 / Accepted: 22 March 2001 / Published online: 31 May 2001
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Abstract Maximum spherical aromaticity occurs in icosahedral fullerenes when the valence π -shells are completely filled with $2(N+1)^2$ electrons. Ab initio calculations of nucleus-independent chemical shifts show that this rule can also be applied to less symmetrical small fullerenes and hydrogen clusters.

Keywords Spherical aromaticity · NICS · $2(N+1)^2$ rule · Fullerenes · Hydrogen clusters

Introduction

The aromaticity of two-dimensional annulenes in singlet ground states follows the Hückel rule, i.e., annulenes with $4N+2$ π electrons are aromatic, while $4N$ π -systems are anti-aromatic. Recently, we have demonstrated that the aromaticity and cluster distortions of the icosahedral fullerenes C_{20} , C_{60} and C_{80} depend on the number of delocalized π electrons in the valence shell, and the resulting $2(N+1)^2$ rule represents the spherical analogy to the $4N+2$ rule for annulenes. [1]

The underlying reason for this rule is that the π -electron system of an icosahedral fullerene can be considered approximately as a spherical electron gas surrounding the surfaces as a sphere in a double skin. The wavefunctions of this electron gas are characterized by the quantum numbers ($l=0, 1, 2, 3$, etc) of their angular momenta. The s shell ($l=0$) is comparable to an atomic s orbital and the shells with $l=1, 2, 3$, etc. are analogous to atomic p, d

and f orbitals, etc. Thus, when all valence shells are completely filled with $2(N+1)^2$ electrons, the skeleton should show no distortions induced by the π -electron system and maximum aromatic character is reached, as demonstrated, for example, by the magnetic properties of C_{20}^{2+} ($l=2$), C_{60}^{10+} ($l=4$) and C_{80}^{8+} ($l=5$). [1]

Although the electron gas model was used to explain the aromatic properties of icosahedral fullerenes, there is no doubt that the spherical aromaticity arising from the π -electron system is a general underlying principle that influences the behavior of all fullerenes. It is reasonable to assume that the $2(N+1)^2$ rule can be applied to a number of less symmetrical fullerenes, as long as their orbitals remain closely related to those of icosahedral fullerenes, and retain the corresponding sub-shell structure in spite of the symmetry reduction. This represents the spherical analogy of the applicability of the Hückel rule to less symmetrical monocycles including heterocycles such as pyridine. It has indeed already been shown that clusters such as C_{32} (D_2) and C_{50} (D_{5h}) obeying the $2(N+1)^2$ rule are very aromatic. [2] In this article we demonstrate that the $2(N+1)^2$ rule holds for a series of less symmetrical fullerenes and related clusters and, moreover, can be used to describe the aromaticity of hydrogen clusters with only delocalized σ electrons.

Computational details

Geometries were fully optimized in the given symmetry at the density functional B3LYP/6-31G* level of theory by using the Gaussian 98 program. [3] The NICS (nucleus-independent chemical shifts) [4] values at the cage centers were computed at the GIAO-SCF/6-31G* level with the B3LYP/6-31G* geometries.

Results and discussion

NICS is known to be a good magnetic measure of aromaticity and is therefore used here to assess spherical aromaticity. Table 1 lists the results for charged carbon clusters with $2(N+1)^2$ π electrons, ranging from C_{16}^{8+} ($N=1$) to

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Table 1 The NICS values (GIAO-SCF/6-31G**/B3LYP/6-31G* at the cage center) of charged carbon clusters with $2(N+1)^2 \pi$ electrons

Species	Symmetry	N_e^a	l^b	NICS
C_{16}^{8+}	D_{4d}	8	1	-58.6
C_{16}^{2-}	D_{4d}	18	2	-32.7
C_{20}^{2+}	I_h	18	2	-73.1
C_{28}^{4-}	T_d	32	3	-35.5
C_{36}^{4+}	D_{2d}	32	3	-64.0
C_{36}^{4+}	C_{2v}	32	3	-57.9
C_{40}^{8+}	D_2	32	3	-62.1
C_{40}^{8+}	D_{5d}	32	3	-82.2
C_{60}^{10+}	I_h	50	4	-81.4 ^c
C_{80}^{8+}	I_h	72	5	-82.9 ^d

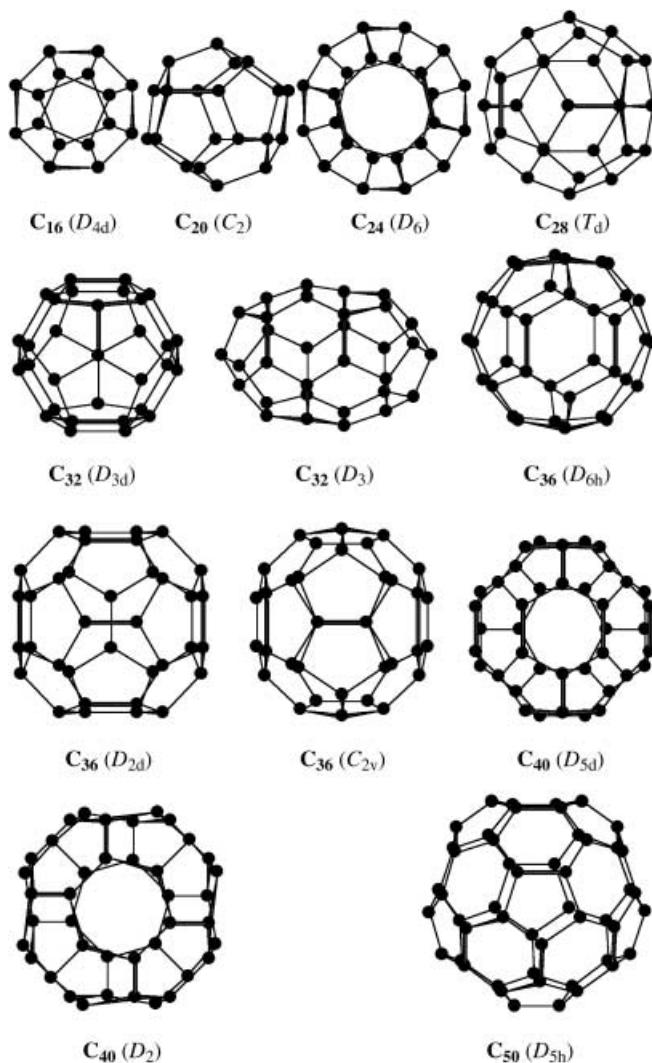
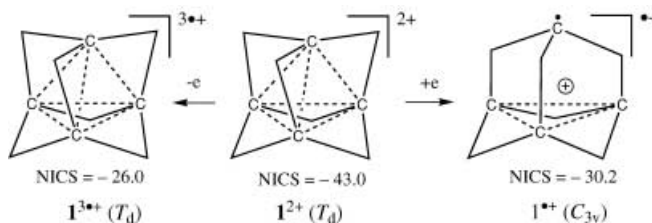
^a Number of the π electrons^b Quantum number l for the closed shells^c GIAO-SCF/3-21G//B3LYP/6-31G* from [1]^d GIAO-SCF/3-21G//HF/6-31G* from [1]**Table 2** NICS values (GIAO-SCF/6-31G**/B3LYP/6-31G* at the cage center) and relative energies (ΔE , kcal mol⁻¹) (from B3LYP/6-31G* total energies) of selected neutral carbon cages

Species	Symmetry	Multiplicity	NICS	ΔE
C_{16}	D_{4d}	Singlet	-1.1	
C_{20}	C_2	Singlet	-36.7	
C_{24}	D_6	Singlet	15.6	
C_{28}	T_d	Quintet	-13.0	
C_{32}	D_3	Singlet	-53.2	0.0
C_{32}	D_{3d}	Singlet	-39.3	73.9
C_{36}	D_{6h}	Triplet	-27.1	0.0
C_{36}	D_{6h}	Singlet	-38.2	3.8
C_{36}	D_{2d}	Singlet	-15.4	0.4
C_{36}	C_{2v}	Singlet	-17.6	7.8
C_{40}	D_2	Singlet	4.0	0.0
C_{40}	D_{5d}	Singlet	2.8	10.6
C_{50}	D_{5h}	Singlet	-37.1	

C_{80}^{8+} ($N=5$). Table 2 collects the data for the neutral carbon clusters studied presently, the chosen isomers being selected on the basis of highest possible stability and symmetry (optimized geometries, see the chart in Figure 1). In the case of C_{20} , the singlet ground state has C_2 instead of I_h symmetry, [1] because of Jahn–Teller distortion. Similarly, the minimum structure of C_{24} is D_6 rather than D_{6d} symmetrical. [5, 6] C_{28} has a quintet ground state with T_d symmetry. [7, 8, 9] Several isomers were considered for C_{32} (D_3 , D_{3d}), C_{36} (D_{6h} , D_{2d} , C_{2v}), and C_{40} (D_2 , D_{5d}). In C_{36} , the ground state is the D_{6h} triplet, [10] but the D_{2d} singlet is almost isoenergetic. [11] In the case of C_{40} , the D_2 and D_{5d} singlet states are the lowest-energy species, [12] whereas the D_{5h} singlet is believed to be the most stable isomer of C_{50} . Generally speaking, it is obvious from Tables 1 and 2 that the carbon clusters with $2(N+1)^2 \pi$ electrons are highly aromatic (highly negative NICS values). In the following, we discuss the systems with $N=1-5$ individually.

N and $l=0$

The smallest polyhedron is the tetrahedron. So far only one example of a tetrahedral carbon-based system with

**Fig. 1.** Chart showing structures of neutral carbon cages**Scheme 1** NICS changes resulting from the removal or addition of electrons to adamantendiyl dication (cited from [13])

spherical delocalization has been identified, the adamantendiyl dication 1^{2+} , in which the HOMO is fully occupied by two electrons (four-center two-electron bonding). As shown in Scheme 1, the addition of one electron results in the monocation 1^{+} and leads to the distortion of the skeleton from T_d into C_{3v} with concomitant reduction of aromatic character. The same is true for the removal of an electron and the formation of the trication 1^{3+} . [13]

N and $l=1$

No systems with eight valence electrons delocalized in three dimensions are known experimentally. One such example with eight π electrons would be the carbon cluster C_{16}^{8+} with D_{4d} symmetry, which contains four-membered rings and is thus not a fullerene. The NICS value for C_{16}^{8+} is -58.6 , much more negative than those of C_{16}^{2+} (-0.3) and neutral C_{16} (-1.1), which have incompletely filled shells.

N and $l=2$

As shown recently, [1] I_h symmetrical C_{20}^{2+} with a NICS value of -73.1 is highly aromatic, whereas its neutral counterpart C_{20} in the singlet state is not only less symmetrical (C_2) but also exhibits much less aromatic shielding (NICS= -36.7). Another example with 18 π electrons is D_{4d} symmetrical C_{16}^{2-} which has a NICS value of -32.7 and is thus much more aromatic than C_{16}^{2+} (-0.3) and neutral C_{16} (-1.1).

N and $l=3$

The first example for $N=3$ is neutral C_{32} . [2] The D_3 isomer is not only more stable than the D_{3d} structure by 73.9 kcal mol $^{-1}$, but also more aromatic. The NICS for the former (-53.2) is more pronounced than that for the latter (-39.3). The tetraanion C_{28}^{4-} (NICS= -35.5) is more aromatic than quintet C_{28} (NICS= -13.0), although both have T_d symmetry. Similarly, the C_{36} tetracations have more negative NICS values (D_{2d} , -64.0 ; C_{2v} , -57.9 ; and the former is 15.3 kcal mol $^{-1}$ more stable than the latter) than the four neutral isomers (Table 2). Whereas the neutral C_{40} species are non-aromatic with NICS of 4.0 (D_2) and 2.8 (D_{5d}), their charged counterparts C_{40}^{8+} have NICS values of -62.1 and -82.2 , respectively. It is interesting to note that the higher symmetrical C_{40}^{8+} (D_{5d}) is more aromatic than the less symmetrical isomer (D_2) because of the difference in spherical distortion, but the former is less stable than the latter by 30 kcal mol $^{-1}$. Therefore, no direct correlation between NICS values and relative energies is found.

N and $l \geq 4$

Examples with higher quantum numbers, e.g., $l=4$ for C_{50} and C_{60}^{10+} , $l=5$ for C_{80}^{8+} have been discussed in our recent paper. [1] Their highly negative NICS values are included in Tables 1 and 2 for comparison.

Hydrogen clusters

In addition to fullerenes, the $2(N+1)^2$ rule is also applicable to three-dimensional hydrogen clusters, e.g., the T_d symmetrical H_4^{2+} and O_h symmetrical H_8 and H_6^{2-} clusters with valence orbitals that are fully occupied by two and eight σ electrons, respectively. The aromaticity of

these clusters [14] has previously been characterized by the computed diamagnetic susceptibility exaltations ($\Lambda=-15.6$ for H_4^{2+} , -21.4 for H_8 and -30.8 ppm cgs for H_6^{2-}) and is now confirmed by the calculated NICS values in the cluster centers, i.e., -22.9 for H_4^{2+} , -52.5 for H_8 and -47.9 for H_6^{2-} . Likewise, the I_h symmetrical H_{20}^{2+} cage with a NICS value of -71.4 is highly aromatic.

Conclusion

In this article, we have given further validation of our recently proposed $2(N+1)^2$ rule. As indicated by the magnetic NICS criterion, spherical aromaticity persists in carbon clusters even after some reduction of symmetry from icosahedral to lower point groups, provided that the π -electron count is correct. The concept of spherical aromaticity is also valid for model hydrogen clusters with delocalized σ electrons.

Acknowledgements This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG). We thank the Alexander von Humboldt Foundation (Z. Chen) and the Centre National de la Recherche Scientifique (CNRS, H. Jiao) for research fellowships.

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