

Local Aromatic Character of C₆₀ and C₇₀ and Their Derivatives

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The ambiguity of the aromatic character of C₆₀ and C₇₀ may result from two reasons: (i) aromaticity is a multidimensional phenomenon and (ii) the local aromatic character of the molecular fragment in question may vary considerably depending on its topological and chemical environment. Application of the aromaticity index HOMA, based on experimental bond lengths, supported (ii): pentagons in fullerenes and their derivatives exhibit very weak or even antiaromatic character, with HOMA values ranging from −0.26 to 0.25. In contrast to that, hexagons exhibit a much larger variation in aromatic character, with HOMA values ranging from 0.1 (anion of C₆₀) to 0.76 in C₇₀6S₈. Pentagons are less aromatic than hexagons, except in the case of C₆₀[−], and C₆₀ is insignificantly less aromatic than C₇₀; both conclusions are in line with magnetic susceptibility studies, the latter also remains in agreement with enthalpy of formation measurements.

INTRODUCTION

Aromaticity is one of the most important general concept for understanding of organic chemistry and of physico-chemical properties of π -electron systems in particular.^{1–4} Hence in the last few decades many quantitative measures of aromatic character have been introduced.^{5,6}

Aromatic character of fullerenes⁷ has been the subject of many studies, yet with no clear cut conclusions.^{8–14} Their rather considerable stability may vote for some aromaticity.¹⁵ However, its enthalpy of formation¹⁶ does not support this idea. Magnetic susceptibility¹⁷ and enthalpy of formation¹⁸ measurements suggest that C₆₀ is less aromatic than C₇₀ and, in general, that the carbon spheroids constitute a class of compounds of “ambiguous” aromatic character.¹⁹ This “ambiguity” may result from two independent factors: (i) aromatic character being a multidimensional phenomenon^{20,21} and hence energetic, geometric, and magnetic properties of a molecule need not be equivalent and (ii) in a general case the aromatic character is not a global property of a molecule since its various fragments may exhibit different aromaticity.²²

RESULTS

In studies of the local aromatic character it is convenient to use the index of aromaticity, HOMA²³ (harmonic oscillator model of aromaticity), which employs experimental bond lengths and describes the degree of alternation of bond lengths in question as well as their deviations from the optimal lengths attributed to the typical aromatic state

$$\text{HOMA} = 1 - \frac{257.7}{n} \sum_{i=1}^n (r_{\text{opt}} - r_i)^2$$

where r_{opt} for CC bonds is 1.388 Å, n stands for the number of bonds in the molecular fragment (or molecule) in question, and 257.7 is a normalization factor to get HOMA = 0 for bond lengths as in butadiene-1,3,²⁴ which is a reference state

for the nonaromatic system and equals 1 for a system with all CC bond lengths equal to the optimal one, 1.388 Å.

The increasing body of experimentally determined geometries of fullerenes and their derivatives encouraged us to apply them to study the local aromatic character of these compounds.

Accepting the I_h symmetry for C₆₀, the situation is simple, and HOMA values calculated from experimental bond lengths²⁵ for pentagons and hexagons are 0.10 and 0.55, respectively. This is in line with strong paramagnetic currents associated with five-membered ring²⁶ and modest diamagnetic shifts by six-membered rings.^{26,27} The HOMA value for the whole molecule equals 0.38 and is in line with small ring current for the whole molecule.²⁶ If the symmetry of the refined model is lowered by using various models of disorder, the number of symmetrically independent pentagons and hexagons increases, and different geometries are found for both kinds of rings. Nevertheless, the HOMA values for the whole molecule for those different models of refinement range between 0.34 and 0.43 and are close to the value obtained for the symmetrical refinement, 0.38. Gas phase electron diffraction gave a slightly different geometry of C₆₀,²⁸ and all HOMA values obtained from it are lower, maintaining the formerly presented regularity: for pentagons −0.26, for hexagons 0.35, and for the whole molecule 0.14. Low values of HOMA for pentagons are in line with their magnetism almost completely quenched by paramagnetic contribution.²⁹

C₆₀ forms a salt with Cs, whose geometry is established.³⁰ HOMA values for pentagons are 0.25, for hexagons 0.13 and 0.10 and for the whole molecule 0.17. In view of the above the following conclusions may be drawn for C₆₀, and its anion are as follows: (i) in C₆₀ pentagons are less aromatic than hexagons, whereas in the anion the reverse is true, (ii) pentagons in C₆₀ and all bonds in its anion exhibit very low or none alternation of bond lengths, thus (iii) if only the alternation of bond lengths is taken to measure aromaticity, i.e., the geometrical indices of aromaticity^{31,32} are applied, then pentagons in C₆₀ and both pentagons and hexagons in C₆₀[−] exhibit aromatic character. This finding is contrary to the results of HOMA estimation and magnetic susceptibility

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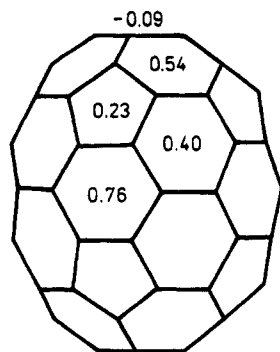


Figure 1. HOMA values for symmetrically independent pentagons and hexagons of C in $C_{70}6S_8$. One molecule of C_{70} is surrounded by 14 molecules of S_8 which are in direct contact with it.

Table 1. HOMA values for some selected molecules or their fragments

molecule or its cyclic fragment	HOMA	comment
benzene	0.99	neutron diffraction at 15 K
Perylene	0.13	X-ray, central ring
	0.81	mean value for other ring which in the crystal lattice are not equivalent, room temp measurement
chrysene	0.50	X-ray, room temp, central rings
	0.86	other rings
6,6-dialkyl derivatives of fulvene	0.00	mean value of 11 structures
6(N,N-dimethyl-amino)-fulvene	0.70	X-ray
cyclopentadienyl anion, Ca salt	0.98	X-ray, two independent molecules
Be salt	0.79	X-ray
C_{60} the whole molecule	0.38	X-ray at 110 K, I_h symmetry
the hexagon rings	0.55	
the pentagon rings	0.10	
C_{60} , the whole molecule	0.14	electron diffraction in the gas phase
the hexagon rings	0.35	
the pentagon rings	-0.26	
C_{60}^- , the whole anion	0.17	X-ray
the hexagon rings	0.10	two kinds of symmetrically independent rings
	0.13	
the pentagon rings	0.25	
$C_{70}6S_8$, the C_{70} moiety	0.39	X-ray

measurements. It is also a substantial support of the idea of multidimensionality^{20,21} of the aromatic character as the observed phenomenon.

A more complicated situation exists in the case of C_{70} , whose geometry is known only for the $C_{70}6S_8$ ³³ complex in which, however, no strong intermolecular interactions are expected. In this case HOMA values for pentagons range from -0.09 to 0.23, whereas for hexagons they are between 0.40 and 0.76, cf. Figure 1 for details. The HOMA value for the whole C_{70} moiety is equal to 0.39, indicating its slightly (but statistically insignificantly) more aromatic character than that of C_{60} , which remains in agreement with literature suggestions.^{18,19} More clear differentiation between C_{60} and C_{70} needs more precise determination of their molecular geometry.

Table 1 presents HOMA values for a collection of pentagons and hexagons taken from selected derivatives of C_{60} and C_{70} for which geometry was determined experimentally. For comparison a few data for pentagonal and hexagonal fragments of typical π -electron systems are added.

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