Rationalizing the relative abundances of trimetallic nitride template-based endohedral metallofullerenes from aromaticity measures†

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The synthesis of endohedral metallofullerenes (EMFs) from a carbon soot sample of an arc discharge leads to a variety of EMFs that are obtained in different relative abundances. In the present work, we show that these abundances can be predicted from aromaticity calculations. In particular, we use the normalized Additive Local Aromaticity (ALA_n) index. Our results show that the most abundant Sc_3N-based and Y_3N-based EMFs in fullerene soot are the most aromatic. This study reinforces the idea that aromaticity plays a key role in determining the stability of EMFs.

Endohedral metallofullerenes (EMFs) have attracted much attention since their discovery because of their extraordinary properties and potential applications. Many different EMFs are obtained by arc discharge or laser vaporization, but only a few of them are produced in macroscopic amounts. The first endohedral metallofullerene obtained in macroscopic quantities was the Sc_3N@C_80 trimetallic nitride template (TNT) EMF, which is the third most abundant fullerene only after C_60 and C_70. The electronic structure of EMFs can be described by the ionic model, as proposed by Poblet and coworkers. When a metallic cluster is encapsulated inside a fullerene cage, a formal charge transfer takes place; thus its electronic structure can be described as M_3N^6+@C_2n. In 2007, Popov and Dunsch showed that hexagonal empty fullerene isomers are good models for describing TNT EMF relative stabilities. Rodriguez-Fortea et al. demonstrated that the negative charge is mainly accumulated in the 5-membered rings (5-MRs) of the carbon structure, and that their distribution along the fullerene surface is crucial for stabilizing the final EMF. In 2015, Martin and coworkers showed that the π-energies obtained from a Hückel molecular orbital (HMO) model are useful to predict the stability of anionic and cationic fullerene isomers. The authors added to the calculated HMO energies an empirical correction of strain energy due to the presence of adjacent pentagon pairs (APPs). Very recently, they demonstrated that the relative isomer stability of anionic fullerenes can be predicted by counting the numbers of three types of hexagon-based motifs and the number of APPs.

A more stable π-electronic structure is likely to be connected with a higher aromaticity. Indeed, it is well-known that the accumulation of negative charge in the 5-MRs of EMFs increases their local and global aromatic character. In 2013, with the goal of understanding the chemical origin of the stability of anionic fullerene cages, we reported an extensive study showing that, for a given C_2n^-m cage, the most stable isomers are the ones whose total aromaticity is maximized, independently of the number of APPs they have. We formulated the maximum aromaticity criterion that gave an explanation for the isolated pentagon rule (IPR) violation in EMFs. In this study, aromaticity measurements were carried out in terms of the Additive Local Aromaticity (ALA) index. We used the HOMA geometric descriptor of aromaticity to reduce the computational cost. Still, the HOMA-based calculations provided aromaticity trends similar to those obtained with more reliable, but computationally more expensive electronic multicenter indices.

Studies of EMF stabilities performed to date analyze the relative stability of isomers of a given C_2n^-m cage. Herein, we have generalized the ALA index to expand its scope and allow the direct comparison of C_2n^-m cages of different sizes. Our aim is to understand the differences in relative abundances in the production of EMFs by arc discharge of metal/graphite rods. To achieve this goal, we propose the normalization of the ALA index per number of rings present in the fullerene structure (ALA_n). Using ALA_n one can compare the aromatics of different fullerene cages regardless of the number of carbons of the fullerene structure (see eqn (1)).

\[ \text{ALA}_n = \frac{1}{n} \sum_{i=1}^{n} A_i \] (1)
Fig. 1 Classification in terms of the ALAN index of selected C_{2n}^{6−} fullerene isomers. The selection was made including the ALA top-ranked C_{2n}^{6−} fullerene isomers for each 2n (see ref. 13): isomers experimentally detected encapsulating TNTs or M2 clusters that formally transfer 6 electrons to the fullerene structure as well as some isomers experimentally detected encapsulating X^{4+} metallic clusters, such as metallic carbides. Isomers experimentally observed forming TNT EMFs are displayed in green, otherwise in red. ALAN values are given in the ALAN_n × 10^4 format.
show the Y$_3$N preference for a non-IPR (22010)-C$_{78}$ cage over an IPR D$_{3h}$-C$_{78}$ isomer. It should be noted that our analysis does not include thermal contributions that have been shown to be necessary to explain the formation and relative abundances of a given isomer at high temperatures. In addition, neither kinetic or mechanistic features nor strain effects on the TNT cluster or C$_{2n}$ cage are included in our predictions. These factors could explain the minor differences between the theoretically predicted EMF ratios based on their ALAN indices and those experimentally observed in an arc discharge synthesis. Nevertheless, the experimental tendency pointing to the major formation of Sc$_3$N-based TNTs I$_h$-C$_{90}$ and D$_{3h}$-C$_{78}$ followed by C$_{68}$ and C$_{78}$ is perfectly reproduced. This result indicates that aromaticity measures in terms of the ALAN index can be used not only to rationalize but also to predict the relative stability (in terms of abundance) of TNT EMFs.

In summary, we proposed a normalized Additive Local Aromaticity index as a measure for the relative stability of any hexaanionic fullerene C$_{2n}$-$^6_6$ isomer regardless of their size (from 2$n$ = 68 to 88, a typical range for TNT EMF formation), or their number of pentagon adjacencies. We have applied our new index (ALAN) to study the relative stabilities of a series of Sc$_3$N-based EMFs. Our results show that Sc$_3$N@I$_h$-C$_{90}$, the most abundant EMF, is also the most aromatic, indicating that aromaticity plays a key role in determining its large stability. Even more, the good agreement between the ALAN values obtained for the Sc$_3$N- and Y$_3$N-based EMF series and the experimental formation ratio indicates that this new measure can be used to understand the chemical origin of the relative stabilities of EMFs, but most importantly to predict their relative abundances.

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Notes and references

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