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Diversity in electronic structure and vibrational properties of fullerene isomers correlates with cage curvature

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ABSTRACT

A theoretical study of pentagon/hexagon-bearing isomers of the C_{32} and C_{86} fullerenes suggests that the diversity in electronic structure and vibrational properties is determined by the surface curvature of the fullerene cage rather than by the global bond network topology. The latter plays a greater role in small, highly constrained fullerene cages, while it can be safely ignored in the case of larger isomers. Selection rules of infrared and Raman spectroscopy are the origin for exceptions from this pattern for bond topologies corresponding to high point-group symmetries of the fullerene cage. The presented data conforms to the common knowledge that discriminating between various isomers of larger fullerenes can constitute a difficult experimental task.

1. Introduction

A fullerene cage can be generated by placing n carbon atoms ($n \geq 20$ and even) on the surface of a (distorted) sphere in such a way that every atom has three closest neighbours located at the distance of typical aromatic C–C bond. For the most important class of carbon fullerenes, i.e., fullerenes containing only pentagon and hexagon rings, this results in an identical local topology characterized by three nearest and 6 s-nearest neighbours of each carbon atom. However, the resulting global topologies of the carbon bonding network can be quite distinct [1,2], constituting the large variation of distinct fullerene isomers for a given n, which tremendously increases with the cage size. The complete classification of conceivable fullerene isomers has been given by Fowler and Manolopoulos [1] (FM) and Brinkmann and Dress [3,4]. The separation process of individual isomers from a mixture of various fullerenes is usually performed using high-performance liquid chromatography (HPLC). The method of choice for identification of various isomers is usually NMR [5–17]; several other techniques has been also applied for this purpose [18–25]. It is natural to expect that each of the isomers would display distinct molecular properties associated with its distinct topological identity. On the other hand, the identical local topology of every fullerene cage may lead to close similarities between the molecular properties of distinct isomers. To investigate the degree in which the local and global topologies influence the molecular fingerprints of fullerenes, we analyse here various molecular properties of all six isomers of C_{32} and selected eighteen isomers of C_{86}. The presented results of this analysis suggest that the global topology of carbon connections has a large effect on the molecular properties only for small, highly-strained fullerene cages, while for larger structures it is almost completely negligible, with possible exceptions for large, tubular fullerenes, for which nanotube-like character may dominate the description of physical and spectral properties. An explanation of the observed regularities is offered and a generalization of our findings is discussed.

2. Computational methodology

The molecular properties of the C_{32} and C_{86} isomers were computed with the self-consistent-charge density-functional tight-binding (SCC-DFTB) method [26,27]. We have used previously this approach to study molecular properties of a variety of fullerenes [28–33] and other carbon nanostructures [34–37]. Benchmark calculations [28] performed for C_{28}, C_{60}, and C_{70} suggested that this approach is of comparable accuracy to DFT methods. Here, we apply SCC-DFTB to assess the following molecular properties for the isomers of C_{32} and C_{86}: distribution of electronic energy levels

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(referred to in the course of text as electronic density of states or EDOS), distribution of vibrational energy levels (referred to as vibrational density of states or VDOS), and infrared (IR) and Raman vibrational spectra. The isomers of C_{32} and C_{86} considered explicitly in the current study are shown in Fig. 1a and b, respectively. In our study we included all conceivable pentagon/hexagon-bearing isomers of C_{32} and 18 (out of 19) conceivable pentagon/hexagon-bearing isomers of C_{86} that obey the isolated pentagon rule (IPR). The results for the C_1 isomer classified by FM as 86:1 are not shown here due to typesetting issues; these results are consistent with the presented here conclusions. For each of the studied isomers, we perform geometry optimization followed by determination of harmonic vibrational frequencies [27,38] and IR [39] and Raman intensities [40]. The EDOS plots were obtained by representing each orbital energy level ε_i by a narrow Gaussian peak centred at ε_i and superposing all such peaks. An analogous procedure was used for obtaining VDOS plots, where the peaks were centred at the computed values of the harmonic vibrational frequencies ν_i. The IR and Raman spectra were obtained in a standard way by a superposition of Gaussian peaks centred at the values of computed harmonic frequencies ν_i and with heights corresponding to the computed IR or Raman intensities.

The average radius of C_{32} isomers is $\overline{r} \approx 2.65$ Å, whereas that of the C_{86} is naturally larger with $\overline{r} \approx 4.31$ Å. The average curvature $\overline{C}$ can be expressed as the inverse of the radius: $\overline{C} = {}^1/_{\overline{r}}$. Obviously, the larger C_{86} fullerenes possess a smaller curvature with $\overline{C}(C_{86}) = 0.232$ Å^{-1} than the smaller C_{32} fullerenes with $\overline{C}(C_{32}) = 0.377$ Å^{-1}. Alternative measures of sp^2 carbon curvature, for instance Haddon's concepts of π-orbital axis vector (POAV) and pyramidalization angle (θ_P) [41,42], give the same obvious result. A graph-theoretical definition of local curvature was used recently to analyse stability of various fullerene cages [43].

3. Results and discussion

The densities of electronic states (EDOS) for the studied isomers of C_{32} and C_{86} are shown in Fig. 2. For the isomers of the smaller fullerene, C_{32}, the resulting EDOS plots have similarly looking spectral envelopes, but the particular features of each plot are distinct. In particular, it would be quite easy to differentiate in experiment between various isomers of C_{32} if their EDOS plots were available. The positions of the Fermi level (EF, here defined as the half-distance between the HOMO and LUMO energies and depicted using red arrows) are similar for each of the isomers, but the

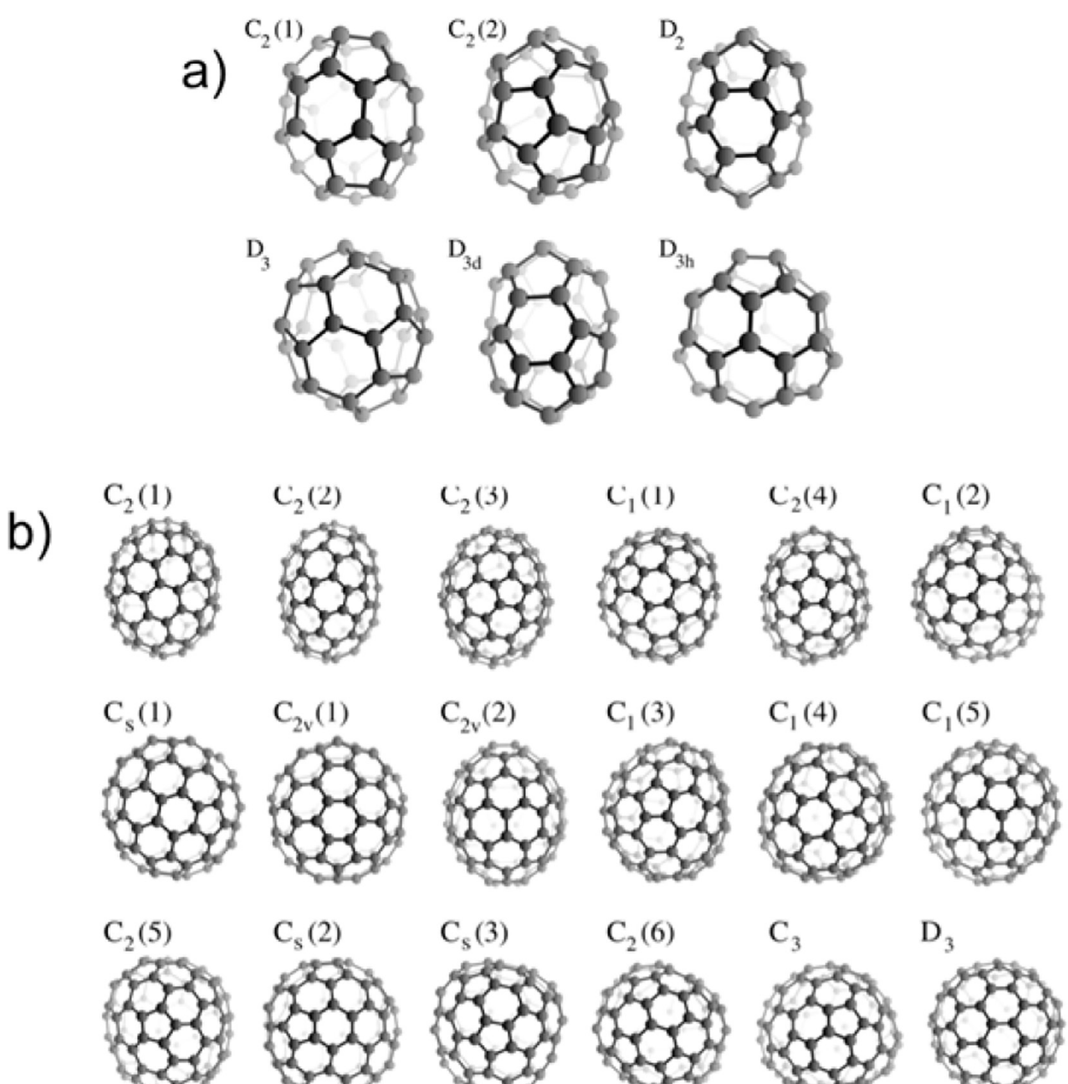

Fig. 1. a) All six isomers of C_{32} and b) selected 18 IPR isomers of C_{86} considered in the current study.