Abstract

Calculations of $^{13}$C nuclear shieldings for low-energy isomers of $C_{36}H_{2x}$ ($x = 2, 3$) suggest that it should be possible to use experimental $^{13}$C shifts, when these become available, to distinguish the isomeric form of the underlying fullerene cage and, in the case of isomers based on the six-fold symmetrical cylindrical fullerene cage 36:15, the degree of polar hydrogenation. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In 1998, Piskoti et al. [1] reported the synthesis of the first solid constructed from a fullerene smaller than $C_{60}$. A year later it was shown by scanning tunneling spectroscopy investigation of the material deposited as a film on a gold substrate, that this $C_{36}$ solid is an insulator [2]. In the first report the mass spectrum of the fullerene containing material showed a signal corresponding to $C_{36}H_6$ rather than bare $C_{36}$, which was taken to indicate high reactivity of the product. $C_{36}$ cages have also been studied on the theoretical level. Fifteen topologically distinct fullerene isomers of $C_{36}$ are possible [3], two of them having the minimum number of 12 pentagon adjacencies and thus offering likely candidates for the stable cages and for the solid made in experiment. The two minimum-adjacency cages (36:14 and 36:15 in spiral nomenclature [3]) are of relatively high symmetry ($D_{2d}$ and $D_{6h}$ respectively). Simple Hückel theory predicts a pseudo-closed shell $\pi$ configuration with a non-zero HOMO–LUMO gap for 36:14. In the case of 36:15, it predicts a zero-gap open shell $\pi$ configuration, which is converted to a closed shell by a second-order Jahn–Teller effect, which leads to a reduction of symmetry to $C_{6v}$ [4] or $C_{2v}$ [5]. 36:14 and 36:15 cages are predicted to be essentially isoenergetic in density-functional based methods [5,6], while Hartree–Fock (HF) and HF based semi-empirical Hamiltonians find 36:14 to be more stable than 36:15 [4,7] by [5]. In most of the ensuing theoretical work on solid $C_{36}$, the 36:15 isomer was taken as the building block [4,8–11]. This choice was based on some experimental indications: namely a $^{13}$C solid state NMR spectrum [1], which is compatible with the spectrum expected of the bare 36:15 cage, though as this spectrum does not show signals for $sp^3$ linking...
atoms, it is difficult to reconcile it with the expectations for a covalent bound fullerene solid [12], and secondly an electron diffraction pattern for the C$_{36}$ solid that suggests hexagonal symmetry [1], which is compatible with the D$_{6h}$ topological symmetry of the 36:15 isomer.

Recently, Koshio et al. [13,14] reported the synthesis of a number of compounds of C$_{36}$, i.e., C$_{36}$H$_4$, C$_{36}$H$_6$, C$_{36}$H$_4$O and C$_{36}$H$_6$O. These molecules are apparently stable species and it can be hoped that in the near future they will become available in quantities appropriate for $^{13}$C NMR characterisation.

Relative stabilities of the isomers of fullerene hydrides with different addition patterns have been considered in previous work. Complete sets of isomers C$_{36}$H$_{2x}$, $x = 0, \ldots, 3$ based on the two underlying cages 36:14 and 36:15 have been studied [15]. Although the bare cages and those with only two hydrogen addends favour 36:14 at the DFTB level, molecules based on the 36:15 cage are found to be of lower energy for C$_{36}$H$_4$ and C$_{36}$H$_6$.

It has been shown for several fullerenes that trends in isomer stability in isostructural series C$_n$H$_m$ and C$_n$F$_m$ are influenced more strongly by the pattern of addition than the identity of the group attached at the sp$^3$ site [16,17]. As the most stable hydrides C$_{36}$H$_4$ and C$_{36}$H$_6$ are based on cage 36:15 rather than 36:14, and as the formation of a polymeric solid will take place by formation of several sp$^3$–sp$^3$ bonds between cages, it seems likely that the more stable C$_{36}$ solids will be based on a 36:15 building block. This isomer has an ideal geometric and electronic structure for the formation of a strong...
lattice composed of hexavalent monomer units [12].

This Letter deals with the question of whether the hydrogenated derivatives $C_{36}H_4$ and $C_{36}H_6$ produced in the experiment of Koshio et al. [13,14] will be identifiable on the basis of their $^{13}$C NMR spectra. We present calculations of $^{13}$C NMR shieldings for the 21 most stable $C_{36}H_4$ and $C_{36}H_6$ isomers as calculated in [15]. Thirteen of these are based on cage 36:14 and eight on cage 36:15. Many
of the studied isomers are of low symmetry, i.e., eight of C\textsubscript{1} and eight of C\textsubscript{s} symmetry. The simulated spectra of these molecules lead to some suggested propensity rules, which connect local structures within the molecules to $^{13}$C NMR signals, which should be of help in identifying structural patterns and the underlying cages from the experimental NMR spectrum, when it becomes available.

2. Computational details

Molecular geometries were generated, optimised and evaluated at the DFTB level [18,19] in a previous study [15]. In the present study, nuclear shieldings were calculated for the carbon nuclei in the selected isomers at these geometries using density-functional theory (DFT) employing a gradient corrected PBE functional [20] with an IGLO-III basis. Calculations were performed using the deMon code [21], which uses auxiliary functions to express the Coulomb potential. It has been found that NMR chemical shifts are sensitive to the choice of auxiliary functions [22] and thus the large A2\textsuperscript{*} set, as implemented in deMon, was selected. Shielding calculations were performed using the deMon-NMR package [23] using uncoupled DF perturbation theory. The accuracy of IGLOIII/A2\textsuperscript{*}/PBE//DFTB calculations has been tested on a set of small hydrocarbons (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and benzene), and maximum deviations from experiment of 4 ppm in the relative shifts with respect to methane were found. Chemical shifts in the present work are calculated with respect to C\textsubscript{60}, which has been treated at the same
level of theory and then referred to experimental shifts with respect to TMS [24].

3. Results and discussion

$^{13}$C NMR patterns of all 21 isomers treated here are presented in Fig. 1. A list of calculated chemical shifts is available from the authors on request. At the most obvious level, inspection of the spectra shows that different addition patterns lead to distinguishable NMR spectra. The molecules with high symmetry give sparse spectra that should be easy to assign; those with low symmetry give more crowded spectra that show a dependence on the underlying cage and on the degree of hydrogenation, even where it may not be possible to resolve individual isomers.

$^{13}$C NMR patterns of fullerenes fall into a range of $\sim$130 to $\sim$150 ppm with respect to TMS [24,25]. In bare fullerenes, all peaks correspond of course to sp$^2$ hybridised carbon atoms. The range moves to higher fields for larger fullerenes, as the average curvature of the cages becomes smaller [24–27]. For C$_{36}$, the $^{13}$C NMR signals of sp$^2$ carbons would be expected to be downfield of C$_{60}$. This expectation is confirmed by NMR calculations at various levels [4,6,28], which predict peaks at $\sim$170 ppm. For the set of isomers presented here the majority of signals are distributed densely in the region of 170 ppm and it is hard to deduce specific isomer information from that region. For the purpose of distinguishing the underlying fullerene cages 36:14 and 36:15, one from another, it turns out be better to concentrate on other parts of the $^{13}$C NMR spectrum.

Once sp$^3$ carbon sites are present in a fullerene, as for example in C$_{60}$ dimer or C$_{110}$, peaks appear in the $^{13}$C NMR spectrum at around 70 ppm downfield of TMS [29,30]. For C$_{36}$H$_{2x}$, this spectral region is indeed very informative. The integrated intensity of sp$^3$ signals gives the degree of hydrogenation. Furthermore as shown in Fig. 2, peaks for isolated sp$^3$ carbon sites are cleanly separated from those adjacent to sp$^3$ sites. The separation is $\sim$20 ppm, with isolated sp$^3$ sites clustering around $\sim$80 ppm, and adjacent sp$^3$ sites with sp$^3$ neighbours appearing $\sim$20 ppm further upfield. As we have seen, these gaps in the spectrum are large compared with the intrinsic uncertainties of the method.

A significant feature, which appears for 36:15 but not for 36:14 based cages, is a group of signals attributable to sp$^2$ carbon sites in positions of high strain in the polar hexagons of the cage. When these polar sp$^2$ sites have no sp$^3$ neighbours, peaks appear at $\sim$200 ppm. The closest sp$^3$ atoms to the polar site are second neighbours, in the (1,4) hexagon belt, which are always present in the low energy forms of hydrogenated or polymerised 36:15 (Fig. 3).

Another set of peaks at $\sim$110 ppm appears only where the underlying cage is 36:15 and this peak can be assigned to polar sp$^2$ carbon sites having sp$^3$ neighbours.

In contrast, the parent cage 36:14 can be recognized by the presence of numerous peaks at $\sim$130 ppm. These peaks arise from various local structures, but do not appear in the 36:15 based cages.

4. Conclusion

This simulation of $^{13}$C NMR spectra of low-energy fullerene hydride isomers C$_{36}$H$_{2x}$ suggest that it will be possible to distinguish the identity of the underlying carbon framework using the experimental $^{13}$C NMR spectra, when these become available. Isomers 36:14 and 36:15 have their characteristic fingerprint peaks, as do sp$^3$ sites in the polar regions of isomers based on the cylindrical 36:15 fullerene.

It will be more difficult to distinguish the precise isomeric form if the molecular symmetry of the experimental isomers turns out to be low. The low-symmetry moieties are at least 34 (39) kJ mol$^{-1}$ less stable than the lowest energy isomer for C$_{36}$H$_4$(C$_{36}$H$_6$) at the DFTB level, and thus possible though not likely on energetic grounds.

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References