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LETTERS

^{13}C NMR Patterns of Odd-Numbered C_{119} Fullerenes

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^{13}C NMR chemical shifts and relative energies of eight C_{119} isomers are calculated within the density-functional-based tight-binding (DFTB) and the IGLO-DFTB (individual gauge for local orbitals) models. The calculated ^{13}C NMR pattern of one C_2 isomer differs considerably from those of other candidates and has a close match with the spectrum of the experimental species. This isomer has also the lowest energy of those studied.

Fullerenes contain even numbers of trivalent, sp^2-like atoms.[1] However, McElvany et al.[2] observed additional odd-numbered species C_{119}, C_{129}, and C_{139} by mass spectroscopy, which are expected to be dimeric structures of C_{60} and C_{70} fullerenes, where several sp^3-like bridging atoms link the two moieties with overall loss of one atom.[3] These molecules can be produced, for example, by reacting fullerenes with ozone[2] or by thermolysis of $C_{120}O$ at 550−600 °C with a yield of ~1%.[4] The C_{119} species has a single predominant isomer for which the ^{13}C NMR spectrum was recorded by Gromov et al.[4] The observed pattern is compatible with an isomer of C_2 symmetry with two signals in the sp^3 carbon region accounting for three (2+1) atoms.

Several approaches have been used to generate plausible topologies of C_{119} isomer candidates. Taylor[5] suggests a construction scheme generating a spiran-like structure of C_s symmetry, which is based on a proposed extrusion mechanism:

$$C_{120}O \rightarrow C_{119} + CO$$

This scheme was generalized by Albertazzi and Zerbetto[6] to produce a total of six candidate isomers, including two of C_2 symmetry. The six isomers are **A**−**F** of Figure 1 and Table 1. They are D_{56}, D_{66}, $4m_{56}$, $4m_{66}$, $5m_{56}$, and $5m_{66}$ in the nomenclature of ref 6 where 4m (5m) means that the connection is via a four- (five-) membered ring, D stands for diversely connected, and the subscript indicates whether the junction involves a pentagon−hexagon or hexagon−hexagon bond. The energetically favored isomer is D_{56} (isomer **A** in this letter).

In a different approach, Adams et al.[7] start from C_{59}, a C_{60} cage with one atom removed, and identify seven possibilities for locating a second C_{60} cage neighboring the defect site; from these initial geometries quantum molecular dynamics (QMD) simulations lead to four final distinct minima. The most stable isomer is again **A**. A simulated Raman spectrum is presented for this isomer in ref 7.

Lebedkin et al.[3] used molecular modeling to produce four low-energy isomers of C_2 symmetry, including the most promising candidate **A** and the second C_2 isomer, **E**. **E** is unstable in the QMD simulations, resulting in a broken-

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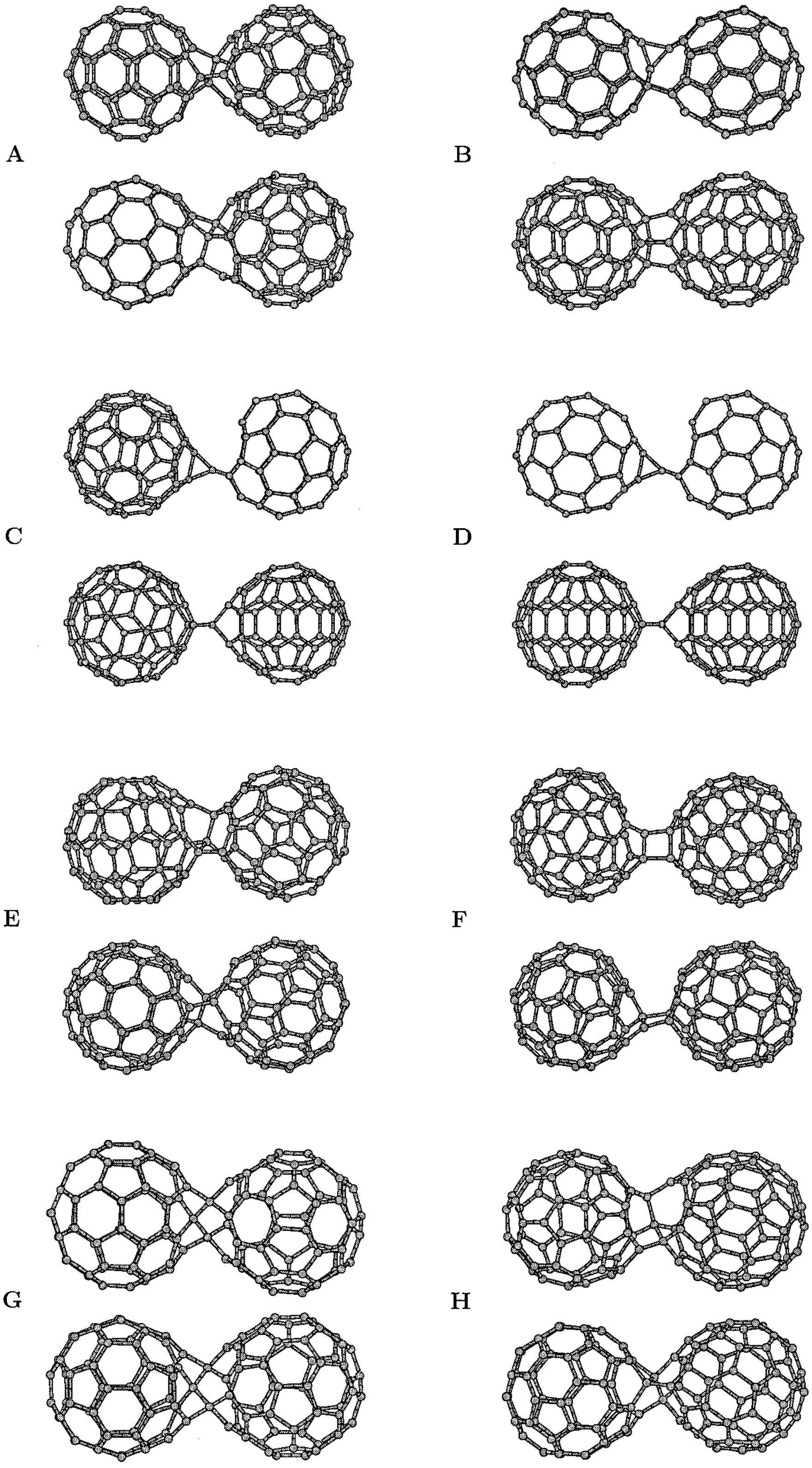

Figure 1. Optimized structures of eight isomers of C_{119}, **A**−**H**. Each structure is shown in plan and elevation.

symmetry C_1 isomer (isomer *III** in ref 3). Calculated energies, and comparison of simulated and measured Raman spectra[3] for the four C_2 isomers again support **A** as the best candidate for the experimentally characterized species.

In the present paper, the eight isomers from ref 6 and ref 3 are compared in energy using the DFTB[8,9] method. ^{13}C NMR patterns for all eight distinct isomers are calculated. The spectra give a clear indication that isomer **A** is indeed the structure produced by Gromov et al.[4]

Geometries and energies are calculated within the DFTB method,[8] parametrized for carbon as in ref 9 which has been tested for various carbon compounds, and found to perform well for fullerenes[10] even though no fullerene data were used in the parametrization process. Initial geometries were taken from

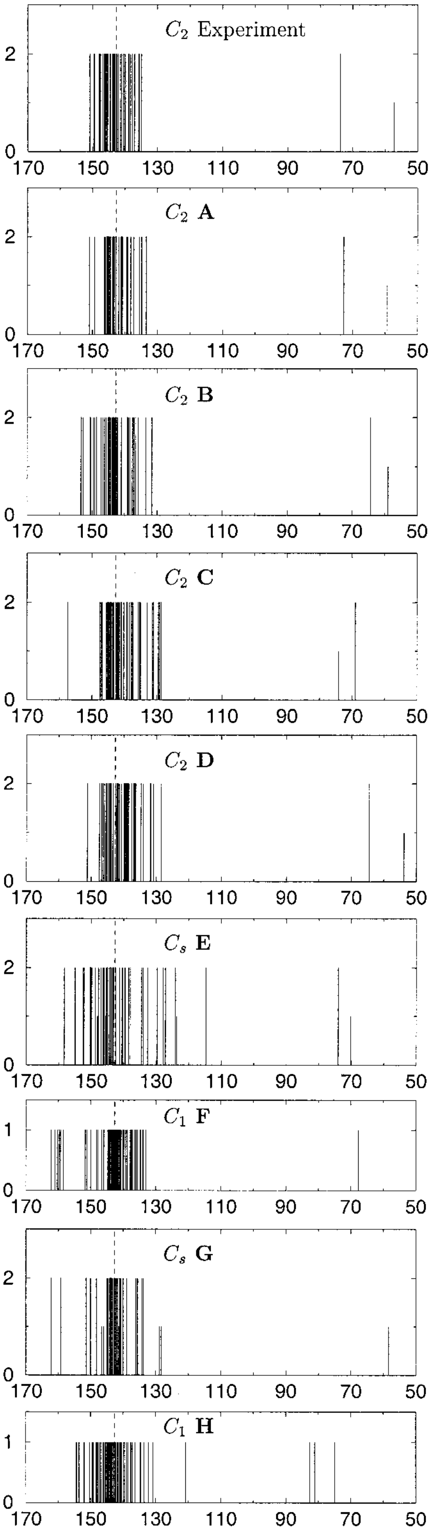

Figure 2. ^{13}C NMR patterns of C_{119} isomers. The idealized experimental C_{119} spectrum (adopted from ref 4) is displayed at the top. **A** includes a signal at 30.7 ppm (half-intensity) and **F** one at 259.1 ppm, resulting from a poor description of this high-energy isomer by a closed-shell configuration. Neither signal is included in the figure. The dashed line gives the position of the C_{60} signal.

TABLE 1: Calculated Energies and ^{13}C NMR Data for C_{119} Isomers[a]

isomers				energies				NMR spectra		
N	N_A	N_L	G	E_M	E_Q	E_D	Δ_G	Δ	$\overline{\delta_{TMS}}$	Δ_{sp^2}
A	D_{56}	*I*	C_2	0.000	0.000	0.000	1.63	91.5	141.9	133.4−150.9
B	D_{66}		C_s	1.514		2.970	0.26	127.6	139.4	114.6−158.3
C	$4m_{56}$		C_1	4.535		4.060	1.54	94.5	142.4	133.1−162.3
D	$4m_{66}$		C_s	3.690		4.250	1.55	103.8	142.2	128.3−162.2
E	$5m_{56}$	*III*	C_2	1.952	2.012	1.982	0.86	88.4	139.1	128.7−157.4
F	$5m_{66}$		C_1	4.615		3.946	0.97	184.1	142.7	120.8−259.1
G		*II*	C_2		2.192	1.926	1.53	94.5	141.2	131.6−153.5
H		*IV*	C_2		1.753	2.163	0.89	97.4	139.4	128.5−151.2
experiment			C_2					93.683	141.537	134.913−150.841

[a] N, N_A, and N_L are codes for the isomers in the nomenclature of this paper, refs 6 and 3, respectively, G indicates the point group. Energies are given relative to the most stable isomer (**A**) at each level, E_M, E_Q, and E_D are the energies (in eV) obtained with the MNDO,[6] QMD,[3] and DFTB methods. Δ_G is the DFTB HOMO− LUMO gap (in eV), Δ the width of the ^{13}C NMR spectrum, $\overline{\delta_{TMS}}$ the position of its center, and Δ_{sp^2} the range of the sp^2 region, all in ppm.

previous calculations[3,6] and optimized employing the steepest descent algorithm without symmetry constraints. ^{13}C NMR chemical shifts were calculated using the IGLO-DFTB model.[11] All parameters are as in ref 11. A uniform scaling (0.75) of the paramagnetic part of the shielding is applied to give the correct difference of the C_{60} shielding and the sp^3 signal of its dimer.[12] Total shieldings are converted to chemical shifts by taking the C_{60} signal as a reference ($\delta_{TMS}(C_{60}) = 142.68$ ppm,[13] see ref 11). IGLO-DFTB parameters, optimized geometries of C_{119}, and their calculated ^{13}C NMR spectra are available as Supporting Information.

The initial topologies are conserved during geometry optimization except in the case of isomer *III** of ref 3 which converges back to **E**. Binding energies are compatible with those from previous MNDO[6] and QMD[3] calculations, as listed in Table 1. The C_2 isomer **A** is clearly favored energetically. The other C_2 isomers from ref 3 are all less stable by ~2 eV, and the isomers of lower symmetry constructed in ref 6 have even higher relative energies. Compared to other carbon species, C_{119}isomer **A** has about the same binding energy per atom as C_{60} and is hence somewhat less stable than $(C_{60})_2$.

Figure 2 compares the experimental[4] and calculated ^{13}C NMR spectra. Most of the isomers including all non-C_2 forms can be excluded as candidates for the characterized C_{119} isomer by the overall pattern of their spectra. The sp^3 signals of the four C_2 isomers are (**A**) 72.7 and 59.4*,(**G**) 64.4 and 59.0*, (**E**) 69.0 and 74.1*, (**H**) 64.6 and 53.8* in IGLO-DFTB, compared with 73.728 and 57.158* in experiment (in ppm, an asterisk indicates half-intensity signals). The range of the sp^2 part of the pattern is given in Table 1. The comparison of these details clearly excludes the three C_2 isomers within the expected tolerance of 5 ppm of the IGLO-DFTB method. The best, and excellent, match in the range of the sp^2 peaks and in the order and position of the sp^3 signals is given by the computed spectrum of **A**.

In agreement with other calculations, the DFTB method finds the isomer **A** (C_2) to be favored energetically among eight plausible candidates for the structure of C_{119}. The calculated ^{13}C NMR chemical shifts are compatible with the experimental spectrum, and identify this isomer as the species obtained experimentally by Gromov et al.[4]

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Supporting Information Available: Cartesian coordinates and calculated chemical shifts of reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes;* Oxford University Press: Oxford, 1995.

(2) McElvany, R. S. W.; Callahan, J. H.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632.

(3) Lebedkin, S.; Rietschel, H.; Adams, G. B.; Page, J. B.; Hull, W. E.; Hennrich, F. H.; Eisler, H.-J.; Kappes, M. M.; Krätschmer, W. *J. Chem. Phys.* **1999**, *24*, 11768.

(4) Gromov, A.; Ballenweg, S.; Giesa, S.; Lebedkin, S.; Hull, W. E.; Krätschmer, W. *Chem. Phys. Lett.* **1997**, *267*, 460.

(5) Taylor, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1629.

(6) Albertazzi, E.; Zerbetto, F. *J. Am. Chem. Soc.* **1996**, *118*, 2734.

(7) Adams, G. B.; Page, J. B.; O'Keeffe, M.; Sankey, O. F. *Chem. Phys. Lett.* **1994**, *228*, 485.

(8) Seifert, G.; Porezag, D.; Frauenheim, T. *Int. J. Quantum Chem.* **1996**, *58*, 185.

(9) Porezag, D.; Frauenheim, T.; Köhler, T.; Seifert, G.; Kaschner, R. *Phys. Rev. B* **1995**, *51*, 12947.

(10) Albertazzi, E.; Domene, C.; Fowler, P. W.; Heine, T.; Seifert, G.; Van Alsenoy, C.; Zerbetto, F. *PCCP* **1999**, *1*, 2913.

(11) Heine, T.; Fowler, P. W.; Seifert, G.; Zerbetto, F. *J. Phys. Chem. A* **1999**, *103*, 8738. The exponent of the DFTB confinement potential is here $n = 2$ as in ref 9.

(12) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583.

(13) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.