

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259353191>

Diastereotopic splitting in the C-13 NMR spectra of sulfur homofullerenes and methanofullerenes with chiral fragments

ARTICLE *in* MAGNETIC RESONANCE IN CHEMISTRY · FEBRUARY 2014

Impact Factor: 1.18 · DOI: 10.1002/mrc.4027 · Source: PubMed

CITATIONS

3

READS

51

3 AUTHORS:



Arthur Tulyabaev

Russian Academy of Sciences

14 PUBLICATIONS 67 CITATIONS

SEE PROFILE



Airat R Tuktarov

Institute of petrochemistry and catalysis of ...

44 PUBLICATIONS 191 CITATIONS

SEE PROFILE



Leonard Khalilov

Russian Academy of Sciences

329 PUBLICATIONS 1,005 CITATIONS

SEE PROFILE

Diastereotopic splitting in the ^{13}C NMR spectra of sulfur homofullerenes and methanofullerenes with chiral fragments

Arthur R. Tulyabaev,* Airat R. Tuktarov and Leonard M. Khalilov

Using gauge-invariant atomic orbital PBE/3 ζ quantum chemistry approach, ^{13}C NMR chemical shifts and diastereotopic splittings of sp^2 fullerene carbons of a number of sulfur homofullerenes and methanofullerenes have been predicted and discussed. An anisochrony of fullerene carbons is caused by a chiral center of attached moieties. Clearly distinguishable diastereotopic pairs (from 8 to 11) of fullerene carbons of homofullerenes were observed. Unambiguous assignments of ^{13}C NMR chemical shifts were performed, and diastereotopic splittings of methanofullerenes were observed for α , β and γ to a functionalization site. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: NMR; ^1H ; ^{13}C ; GIAO PBE/3 ζ ; sulfur homofullerenes and methanofullerenes; diastereotopicity

Introduction

A full and unambiguous assignment of fullerene resonances observed in ^{13}C NMR spectrum has been carried out successfully first for the osmylated C_{60} .^[1,2] To perform INADEQUATE NMR experiments with the appropriate sensitivity, a fullerene sample enriched with a ^{13}C isotope was used. The ^{13}C NMR spectrum of the osmylated C_{60} contained 17 fullerene signals. This conforms to the case that the molecule possesses two orthogonal mirror planes. ^{13}C NMR signal assignment, as well as a relationship between the ^{13}C – ^{13}C couplings and corresponding bond lengths obtained with the X-ray, has been carried out. Similarly, using ^{13}C -enriched fullerene samples, the authors provided a detailed description of the structure of simple homofullerenes and methanofullerenes.^[3–5] Moreover, structure elucidation of these derivatives was performed using direct ^1H – ^{13}C couplings of methylene groups, which then were compared with the corresponding bond lengths of methano-bridged annulenes. Signal assignment in the ^{13}C NMR spectra of numerous C_{60} bis-adduct regioisomers is quite difficult. To solve the problem, ^{13}C -labeled fullerene samples were also required. They were used to generate bis-methano[60]fullerenyl amino acid derivatives,^[6–8] bis-germylated cycloadducts^[9] and 1,16-dialkyl-1,16-dihydro[60]fullerenes.^[10] With these assignments, it was possible to identify a relative arrangement of the attached moieties within a fullerene hemisphere. Attribution of fullerene carbon resonances observed in the ^{13}C NMR spectra and careful considerations of C–C bonds lengths and dihedral angles of fullerene cage of the 1,2-methano[60]fullerene 61,61-dicarboxylate were performed.^[11] The data obtained with X-ray technique were compared with $^1J(\text{C},\text{C})$ values extracted from the INADEQUATE spectrum of the isotopically enriched fullerene derivative, and it was possible to correlate the topological distortion of the fullerene cage due to cyclopropanation. Using the hydrogenated fullerenes C_{60}H_2 and C_{60}H_6 as references, it was shown that the most high-frequency signals in their ^{13}C NMR spectra correspond to sp^2 carbons directly attached to sp^3 carbons.^[12] The

authors identified an interesting pattern that, in turn, the most low-frequency signals belong to the carbon atoms coupled to those that resonate in high-frequency region. They assumed that such a displacement of resonances toward these regions is attributed with the appearance of a new ring current pattern in comparison with a pure C_{60} .

The different types of relationships were considered in detail for both hydrogenated fullerenes. Experimental ^{13}C – ^{13}C coupling constants and calculated C–C bond lengths correlate with the pyramidalization angle and ^{13}C chemical shifts calculated as well as experimental ^{13}C chemical shifts. A series of ^{13}C -labeled fullerene derivatives with three-membered, four-membered and five-membered annulated rings were synthesized.^[13] The authors consistently found that there is no a strong interrelation between the dispersion of fullerene carbon signals in the ^{13}C NMR spectrum and the local strain caused by the annulated cycle; in addition, a correlation between this dispersion and pyramidalization angle does not exist. However, they assumed that there is a strong evidence for a paramagnetic ring current circulating around the site of an addition.

In recent years, quantum chemical methods were developed to ascribe the signals in the ^{13}C NMR spectra of fullerene derivatives.^[14–16] However, it should be noted that literature does not contain many papers on theoretical modeling of ^{13}C chemical shifts with quantum chemistry approaches. Previously, we used the gauge-invariant atomic orbital (GIAO) PBE/3 ζ method to predict signals of the ^{13}C NMR spectra of spiro C_5 homofullerenes and C_{2v} methanofullerenes,^[17] and C_1 spiro homofullerenes and methanofullerenes with chiral moieties attached.^[18] However, no work has been reported concerning the influence of chiral elements on the fullerene skeleton in fullerene derivatives with

* Correspondence to: Arthur R. Tulyabaev, Institute of Petrochemistry and Catalysis, 141 Pr. Oktyabrya, Ufa, Russia, 450075. E-mail: tulebeich@gmail.com

Institute of Petrochemistry and Catalysis, 141 Pr. Oktyabrya, Ufa, Russia, 450075

heteroatoms. In this context, the purpose of the present work is to establish an influence of chiral elements in attached moieties on the fullerene core and to predict ^{13}C NMR chemical shifts and diastereotopic splittings of a number of sulfur homofullerenes and methanofullerenes.

Results and Discussion

According to the schemes described earlier in the articles, sulfur homofullerenes **1–5** and methanofullerenes **6–13** (Fig. 1) have been synthesized.^[19,20] First, we carried out an assignment of ^1H and ^{13}C NMR spectra of the attached moieties by combining two-dimensional homonuclear and heteronuclear correlation NMR techniques (see supporting information). Further, the structure features of fragments would allow an understanding of its immediate effect upon the fullerene core.

Thereby, we decided that every attached fragment of all discussed sulfur fullerene derivatives **1–9** contains one chiral carbon.

Consider the simplest homofullerene C_{61}H_2 that has been first obtained and discussed by Wudl and co-workers.^[5] As a rule, the ^{13}C NMR spectrum of this compound contained 31 resonances of sp^2 fullerene carbons in the range $\delta = 135.15\text{--}149.25$ ppm. This conforms to the case that the molecule can be divided into two mirror parts and can be assigned to C_s point group symmetry, which is characteristic for the achiral molecules. Certainly, both fullerenyl parts contain 28 carbons, whereas the rest of the four carbons lie in a mirror plane. At the same time, the spiro homofullerene **14** obtained in our institute is a similar compound. It is confirmed by the fact that the ^{13}C NMR spectrum of **14** contained 30 resonances in the range $\delta = 135.20\text{--}147.50$ ppm, and 26 of them had double intensities (2C); three resonances $\delta = 135.83$, 142.96 and 144.52 were of single intensity

(1C); that at $\delta = 142.06$ was a fivefold intensity signal (5C). Thus, **14** also possesses C_s point group symmetry. In this regard, both C_{61}H_2 and **14** may be used as reference compounds to compare them with the **1–5** and to estimate how chiral centers of attached fragments influence the fullerene core. Moreover, to calculate ^{13}C NMR chemical shifts of considered fullerene derivatives, we used the GIAO PBE/3 ζ quantum chemistry approach.^[21,22]

In order to estimate the diastereotopicity of fullerene carbons, we compared directly the ^{13}C NMR spectra of reference and fullerene derivatives with chiral fragments in the similar ranges. So, ^{13}C NMR spectrum of spiro homofullerene **14** contained peaks of 2C intensity $\delta = 147.48$, whereas in ^{13}C NMR spectrum of the fulleroid **1** in a similar range, there were revealed two anisochronous resonances of 1C intensity $\delta = 147.41$ and 147.48, of the **2** – $\delta = 147.42$ and 147.50, of **3** – $\delta = 147.31$ and 147.36, of **4** – $\delta = 147.31$ and 147.36, and of **5** – $\delta = 147.26$ and 147.31. Obviously, such signal splitting is explained by the anisotropic influence of the C-2' chirality center in the attached moiety. This was not observed for the **14** and the simplest fulleroid C_{61}H_2 . The reason of chemical shifts nonequivalence is the so-called 'unequal' susceptibility of magnetic field by either diastereotopic nuclei.^[23–29] To estimate this effect quantitatively, there is a diastereotopic splitting $\Delta\delta_{\text{dias}}$, which is 0.07 ppm for **1**, 0.08 ppm for **2**, and 0.05 ppm for **3**, **4** and **5**. According to quantum chemistry calculations, the aforementioned signals are attributed to sp^2 C-3/C-4 fullerene carbons. These atoms are two chemical bonds away from the C-2' chirality center. Similarly, nine pairs of the splitted signals were observed in the ^{13}C NMR spectrum of **1** (Fig. 2).

As can be seen from Table 1, the magnitude of diastereotopic splitting for this molecule is different and depends on that how far a chiral carbon in the attached fragment is away from the fullerene core. Furthermore, the influence of the C-2' asymmetric carbon is spread over the whole fullerene moiety. For example, the diastereotopic carbons C-56/C-59 (Fig. 3) are seven bonds away

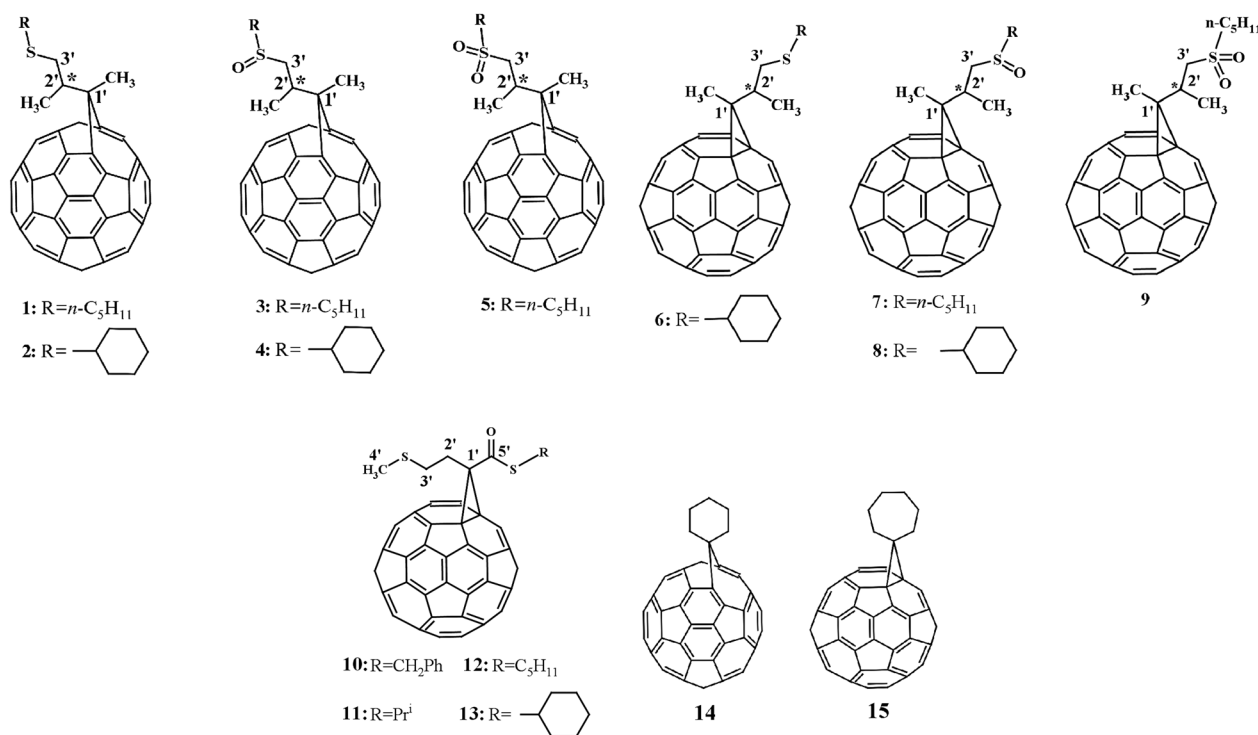


Figure 1. Sulfur homofullerenes **1–5**, methanofullerenes **6–13** and the reference fullerene derivatives **14** and **15**.

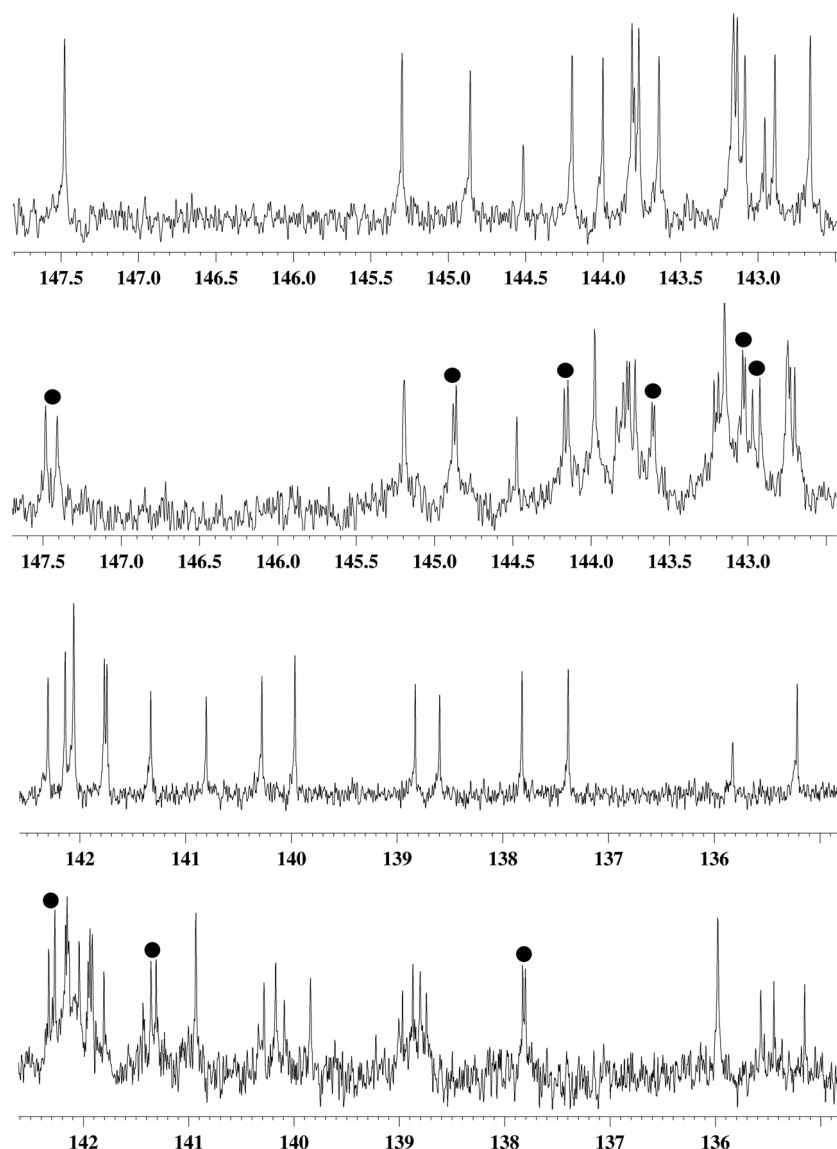


Figure 2. Comparison of the ^{13}C NMR spectra of the reference **14** (**11** in article^[17] – top) and homofullerene **1** (bottom). The pairs of diastereotopic resonances are depicted with circles.

from the site of addition, and $\Delta\delta_{\text{dias}}$ is 0.05 ppm, which is quite comparable with the magnitudes of C-3/C-4 (0.05–0.08 ppm).

On the whole, the ^{13}C NMR spectrum of the fulleroid **1** comprised 44 resonances: 33 of these signals were 1C intensity, six had 2C intensity and remaining five were of 3C intensity. The signals of 2C and 3C intensities were formed from the isochronous peaks of 1C intensity and, therefore, overlapped. For example, multiplet resonances were observed in all sections of the ^{13}C NMR spectrum of **1** (see supporting information).

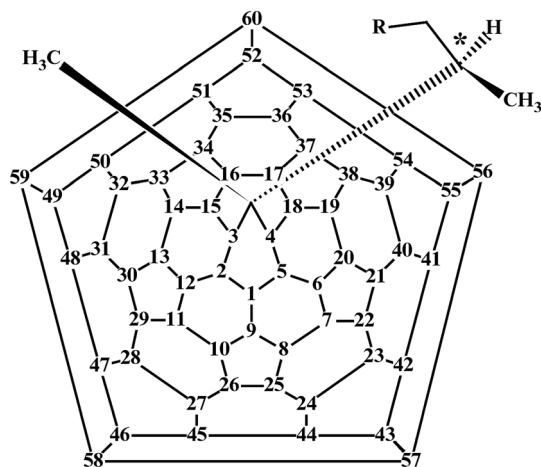
Next, 50 resonances were revealed in the ^{13}C NMR spectrum of **2**: 43 of them were identified with 1C intensity, six carbons as 2C and one is a 5C intensity signals. Eleven diastereotopic pairs of distinguishable sp^2 carbons were observed. As seen from Table 1, the diastereotopic splittings did not affect the same carbons of **1** and **2** (e.g. C-8/C10 or C-6/C-12, etc.) because of quite different patterns of attached moieties. The fullerenyl sp^2 region of the ^{13}C NMR spectrum of **3** contained 44 peaks: 34 of them had 1C intensity, three had 4C and seven were of 2C intensity. The eight diastereotopic carbon pairs of this compound were obvious. The ^{13}C NMR

spectrum of **4** has shown 40 signals of a fullerene core that were registered at $\delta = 135\text{--}147$ ppm. 29 peaks were of 1C, seven were as 2C, three were of 4C and one resonance was of 5C intensity. Comparing its ^{13}C spectrum with that of **14**, it is clear that there are 10 diastereotopic pairs of fullerenyl carbons. Finally, ^{13}C NMR spectroscopy of **5** revealed 45 signals and 10 pairs of splitted signals of them. Thus, the diastereotopic splittings for C-3/C-4 atoms are clear for all the homofullerenes **1–5**, but a diastereotopicity of the other anisochronous carbons does not occur in all the cases.

The simplest methanofullerene C_{61}H_2 obtained by Smith III and co-workers^[3,4] is assigned to a C_{2v} point group symmetry. This pattern of symmetry contains the only a second order axis C_2 and two orthogonal planes that cross along it.^[28] Such a finding is based on a fact that ^{13}C NMR spectrum of C_{61}H_2 contained 16 sp^2 fullerenyl resonances of various intensity in range of $\delta = 136.5\text{--}149.5$ ppm. Later, Meier *et al.* provided assignments of ^{13}C NMR spectra of the simplest hydrofullerenes C_{60}H_2 and C_{60}H_6 , methanofullerene C_{61}H_2 and $[2+2]$ and $[2+3]$ cycloadducts.^[12,13]

Table 1. Diastereotopic pairs of fullereryl carbons in **1–5**

14	1	2	3	4	5
135.06 (C-14/C-19)				135.02/135.07 (0.05)	135.10/135.16 (0.06)
135.89 (C-7/C-11)		136.00/136.04 (0.04)			
137.82 (C-8/C-10)	137.81/137.83 (0.02)		137.92/137.96 (0.08)	137.91/137.97 (0.06)	
138.79 (C-6/C-12)		138.84/138.89 (0.05)			
138.98 (C-2/C-5)				139.02/139.09 (0.07)	138.98/139.07 (0.09)
139.55 (C-21/C-30)			139.89/139.92 (0.03)	139.18/139.25 (0.07)	139.14/139.36 (0.12)
140.18 (C-35/C-36)		140.10/140.19 (0.09)	141.07/141.17 (0.10)	139.89/139.92 (0.03)	140.41/140.43 (0.02)
141.53 (C-31/C-40)	141.31/141.36 (0.05)				141.31/141.45 (0.14)
141.97 (C-13/C-20)		141.88/141.92 (0.04)			
142.22 (C-41/C48 or C-57/C58)		142.13/142.17 (0.04)	142.15/142.18 (0.03)		
142.30 (C-43/C-46)	142.27/142.30 (0.03)	142.29/142.33 (0.04)			142.37/142.54 (0.17)
142.76 (C-25/C-26)		142.75/142.79 (0.04)	142.76/142.80 (0.04)	142.70/142.76 (0.06)	
142.96 (C-56/C-59)	142.92/142.97 (0.05)	142.93/142.98 (0.05)			
143.08 (C-34/C-37)	143.03/143.07 (0.04)			143.02/143.09 (0.07)	
143.54 (C-24/C-27)	143.59/143.61 (0.02)				
143.70 (C-49/C-55)					143.70/143.73 (0.03)
144.00 (C-32/C-39)			143.99/144.04 (0.05)	143.98/144.03 (0.05)	
144.20 (C-32/C-39)	144.15/144.17 (0.02)	144.16/144.18 (0.02)	144.20/144.25 (0.05)	144.20/144.25 (0.05)	144.25/144.29 (0.04)
144.86 (C-22/C-29)	144.86/144.88 (0.02)				
145.25 (C-33/C-38)		145.21/145.24 (0.03)			145.07/145.20 (0.13)
147.56 (C-3/C-4)	147.41/147.48 (0.07)	147.42/147.50 (0.08)	147.31/147.36 (0.05)	147.31/147.36 (0.05)	147.26/147.31 (0.05)

**Figure 3.** Schlegel diagram of the homofullerenes **1–5** with numbered carbons.

In view of these observations, consider the methanofullerenes **6–9**. Because of the structure of attached moieties, different amounts of the resonances exist in the range of $\delta = 137$ – 148 ppm of ^{13}C NMR spectra of compounds **6–9**. sp^3 fullereryl carbons as a rule resonate at $\delta = 70$ – 90 ppm (see supporting information). So, the spectrum of **6** contained 31 signals: eight peaks had 1C intensity, 21 were of 2C and two were of 4C resonances. Thirty-six signals of **7** were revealed: 22 with 1C intensity, 12 had 2C and two had 7C intensity. The ^{13}C spectrum of **8** included 38 signals of the sp^2 anisochronous fullereryl carbons: 23 were of 1C intensity, 14 had 2C and one had 7C intensity. Finally, compound **9** showed 26 distinctive fullerene carbons in the ^{13}C NMR spectrum. Such anisochrony of the fullerene core is caused by the influence of the C-2' carbon of

attached fragment. A suitable reference compound to estimate an anisochrony of a fullerene moiety quantitatively is methanofullerene (**15**). A comparison of the ^{13}C NMR chemical shifts of the similar ranges of **15** with the methanofullerenes **6–9** is given in Table 2.

A fullerene moiety of **15** contains 13 sorts of magnetically equivalent carbons, and each one includes four atoms; this is confirmed by the fact that there are 13 resonances with 4C intensity. Three peaks with 2C intensity mean that there are three other kinds of sp^2 fullereryl carbons. The resonance $\delta = 148.74$ ppm can be compared with four signals of methanofullerene **6** $\delta = 147.42$, 147.58 , 148.60 and 148.62 ppm. According to quantum chemistry calculations, these peaks were assigned to α C-2, C-5, C-8 and C-10 of the fullerene core. We suggest estimation of a diastereotopicity $\Delta\delta_{\text{dias}}$ of a fullerene moiety finding a relative difference of the ^{13}C chemical shift values in a similar range of a spectrum between the reference compound **15** and the discussed methanofullerene. Thus, for the carbons C-2, C-5, C-8 and C-10 of **6**, $\Delta\delta_{\text{dias}}$ are 1.32, 0.16, 1.02 and 0.02 ppm. For **7**, these values are 1.51, 0.14, 0.54 and 0.45 ppm; for **8**, they are 1.40, 0.03, 0.61 and 0.33, and finally, they are 1.84, 0.38, 0.07 and 0.83 ppm for **9**. The β carbons C-6, C-7, C-11 and C-12 of **15** resonate as the 4C peaks at $\delta = 137.60$ ppm. This signal can be contrasted to four different resonances with 1C intensity of compound **7**; therefore, $\Delta\delta_{\text{dias}}$ are 0.07, 0.08 and 0.39 ppm, $\Delta\delta_{\text{dias}}$ 0.04, 0.03, 0.38 and 0.02 ppm for **8**, and 0.02, 0.09, 0.15 and 0.22 ppm for **9**. Similar $\Delta\delta_{\text{dias}}$ values have been obtained for γ C-15/C-18/C-24/C-27 atoms, which are 0.04, 0.03, 0.07 and 0.15 ppm for **6** and 0.02, 0.11, 0.08 and 0.07 for **7**; for methanofullerene **8**, they are 0.09, 0.02, 0.01 and 0.03 ppm and, finally, are 0.08, 0.16, 0.20 and 0.13 for the compound **9**. In the other ranges of the ^{13}C NMR spectra of **6–9**, overlapped resonances of the sp^2 anisochronous fullereryl carbons were observed. Therefore, the diastereotopic splittings cannot be derived unequivocally and unambiguously. So, we were able to estimate a

Table 2. Comparison of ^{13}C NMR chemical shifts of **15** with **6–9** (CDCl_3 , at 298 K; the unresolved resonances are designated with asterisks)

15	6	7	8	9	15	6	7	8	9
137.60 (4C)	*	137.67	137.64	137.58	144.22 (4C)	143.99	143.78	143.77	143.25
		137.75	137.70	137.76		143.99	143.82	143.77	143.25
		138.14	138.13	137.90		144.17	144.33	144.26	144.35
		*	138.16	137.92		144.17	144.33	144.26	144.35
140.99 (4C)	140.95	140.97	140.90	141.07	144.40 (2C)	144.28	144.38	144.30	144.40
	140.98	141.06	140.97	141.11		144.28	144.38	144.42	144.40
	141.05	141.06	140.99	141.18	144.78 (4C)	144.43	144.45	144.46	144.51
	141.20	141.12	141.08	141.18		144.43	144.49	144.46	144.51
142.21 (4C)	142.03	142.11	142.10	142.12		144.81	144.82	144.78	144.87
	142.19	142.19	142.10	142.12		144.81	144.82	144.78	144.87
	142.26	142.25	142.16	142.17	144.99 (2C)	144.90	144.86	144.82	144.87
	142.67	142.25	142.16	142.17		144.90	144.86	144.82	144.87
142.26 (4C)	142.75	142.27	142.22	142.17		144.95	144.97	144.97	144.87
	142.94	142.27	142.27	142.24		144.95	144.97	144.97	144.87
	142.97	142.30	142.31	142.24	145.11 (4C)	145.17	145.18	145.13	145.23
	142.97	142.30	142.37	142.24		145.17	145.18	145.13	145.23
143.05 (4C)	143.05	143.10	143.05	143.16		145.17	145.27	145.22	145.27
	143.05	143.10	143.05	143.16		145.21	145.27	145.22	145.27
	143.09	143.10	143.05	143.16	145.24 (4C)	145.21	145.27	145.26	145.32
	143.09	143.10	143.05	143.16		145.21	145.27	145.26	145.32
143.11 (4C)	143.15	143.10	143.05	143.16		145.21	145.27	145.49	145.39
	143.15	143.10	143.05	143.16		145.27	145.27	145.53	145.39
	143.15	143.13	143.05	143.16	145.72 (4C)	145.27	145.47	145.60	145.44
	143.15	143.13	143.14	143.16		145.27	145.52	145.60	145.44
143.20 (2C)	143.63	143.17	143.14	143.25		145.27	145.61	145.76	145.48
	143.63	143.17	143.17	143.25		145.27	145.74	145.76	145.48
143.77 (4C)	143.74	143.22	143.17	143.25	148.74 (4C)	147.42	147.23	147.34	146.90
	143.74	143.26	143.22	143.25		147.58	147.28	147.39	147.04
	143.80	143.73	143.70	143.25		148.60	148.12	148.19	147.65
	143.80	143.73	143.70	143.25		148.62	148.15	148.27	147.77

diastereotopicity only for neighboring environments (α , β and γ) relative to the functionalization site of a fullerene core.

Considering methanofullerenes **10–13**: as follows from the ^1H and ^{13}C NMR assignments, the attached fragments of these compounds do not contain any asymmetric carbon, but two sulfur atoms. In this regard, there are only 24 resonances with different intensity (18 signals are 2C, three have 3C, two are 4C and one 5C intensity) in the ^{13}C NMR spectra (Fig. 4).

As seen from the spectra in Fig. 4, a signal $\delta = 137.60$ ppm of **15** can be compared with two splitted resonances of all the methanofullerenes **10–13**, such as $\delta = 136.87$ and 138.11 ppm for **10**, $\delta = 137.59$ and 138.06 ppm for **11**, $\delta = 137.60$ and 138.08 ppm for **12** and $\delta = 137.57$ and 138.06 ppm for **13**. According to quantum chemistry calculations, these peaks correspond to sp^2 fullereryl C-6/C-7/C-11/C-12 atoms. The diastereotopic splittings $\Delta\delta_{\text{dias}}$ given in Table 3 have been estimated similarly, as for the **6–9**.

According to quantum chemistry calculations, the resonance $\delta = 140.99$ ppm is referred to sp^2 fullereryl C-15/C-18/C-24/C-27 atoms; in addition, $\delta = 143.77$ and 145.72 ppm correspond to C-33/C-38/C-42/C-47 and C-3/C-4/C-25/C-26, respectively. The other peaks are overlapped, and precision assignments are required here. For example, the signals $\delta = 142.21$ and 142.26 ppm of **15** are contrasted to complex overlapping signals in the range $\delta = 142.0$ – 142.5 ppm of the methanofullerenes **10–13**. The same is characteristic for the overlapped peaks in the section $\delta = 142.5$ – 146.0 ppm.

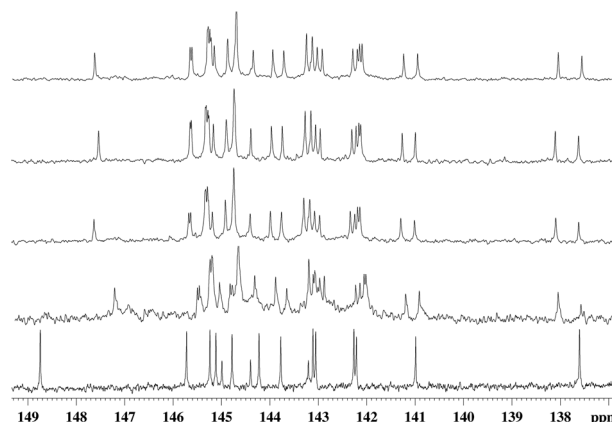


Figure 4. ^{13}C NMR spectra of the reference **15** (bottom) and the methanofullerenes **10–13** (the expanded fullereryl region $\delta = 137$ – 149 ppm is shown).

Thus, we were able to measure the chemical shifts and diastereotopic splittings for the methanofullerenes **10–13** that include two sulfurs in attached moieties. These effects have unequivocally been estimated for α , β and γ to the functionalization site.

Table 3. ^{13}C NMR chemical shifts and diastereotopic splittings $\Delta\delta_{\text{dias}}$ of **10–13**; values of $\Delta\delta_{\text{dias}}$ in parentheses

15	10	11	12	13
137.60	136.87 (0.73)	137.59 (0.01)	137.60 (0)	137.57 (0.03)
	138.11 (0.51)	138.06 (0.46)	138.08 (0.48)	138.06 (0.46)
140.99	140.98 (0.01)	140.98 (0.01)	140.97 (0.02)	140.96 (0.03)
	141.26 (0.27)	141.27 (0.28)	141.24 (0.25)	141.25 (0.26)
143.77	143.72 (0.05)	143.73 (0.04)	143.72 (0.05)	143.73 (0.04)
	143.95 (0.18)	143.96 (0.19)	143.94 (0.17)	143.95 (0.18)
145.72	145.52 (0.20)	145.61 (0.11)	145.60 (0.12)	145.62 (0.10)
	145.56 (0.16)	145.65 (0.07)	145.62 (0.10)	145.66 (0.06)

Conclusions

In summary, ^{13}C NMR chemical shifts have been predicted and assigned, and it has been shown that there are diastereotopic splittings of the sp^2 fullerene carbons in a number of sulfur homofullerenes and methanofullerenes. It has been ascertained that such a splitting of **1–9** is caused by the influence of the chiral carbon included in attached fragments. This effect is spread not only over the neighboring environment but also over the whole fullerene core. For the methanofullerenes **6–13**, diastereotopic splittings $\Delta\delta_{\text{dias}}$ have been estimated corresponding to α , β and γ to the functionalization site. The other core carbons resonate as the complex overlapped multiplets that can be distinguished with precision NMR INADEQUATE techniques.

Experimental

The homofullerenes **1–5** and the methanofullerenes **6–13** have been prepared according to methods described earlier.^[19,20]

Full geometry optimization and vibration frequency analysis of the fullerene derivatives were performed in the PBE/3 ζ approach^[30–32] (PRIRODA program^[33]). The ^{13}C NMR chemical shifts were calculated for the thermodynamically stable conformations of the fullerene derivatives using the GIAO method^[34] relative to the Me_4Si as internal standard (absolute ^1H and ^{13}C chemical shift values are -31.3917 and -182.0037 , respectively) and taking into account the correction of the experimental ^{13}C chemical shift value of the unsubstituted fullerene C_{60} ($\delta = 143.15$ ppm).^[35] The C_{60} fullerene carbons have been numbered in accordance with the IUPAC recommendations.^[36]

One-dimensional (^1H and ^{13}C) and two-dimensional (COSY, HSQC and HMBC) NMR spectra were recorded on a Bruker Avance 400 (Karlsruhe, Germany) (400.13 MHz for ^1H and 100.62 MHz for ^{13}C) at 298 K in 5 mm outer diameter tubes. The chemical shifts were internally referenced to CDCl_3 signals ($\delta = 7.28$ ppm for ^1H and $\delta = 77.0$ ppm for ^{13}C). The pulse conditions were as follows: for the ^1H NMR spectra, 90° pulse flip angle, acquisition time (AQ) = 2.05 s, high-power pulse (P1) = 8.00 μs , spectral width (SW) = 4000 Hz, data points (TD) = 16 384, number of scans = 32; for the ^{13}C NMR spectra, 30° pulse flip angle, P1 = 4.7 s, AQ = 0.9 s, dummy scans = 2, relaxation delay (RD) = 1.0 s, SW = 18 116 Hz, TD = 32 768; for the COSY spectrum, AQ = 0.32 s, RD = 0.84 s, SW = 1600.5 Hz, TD = 1024 \times 128; for the HSQC spectrum, AQ = 0.32 s, RD = 0.84 s, SW (F1) = 7043.1 Hz, SW (F2) = 1600.5 Hz, TD = 1024 \times 128;

for the HMBC spectrum, AQ = 0.32 s, RD = 0.84 s, SW (F1) = 18 115.9 Hz, SW (F2) = 1600.5 Hz, TD = 1024 \times 128.

References

- [1] J. M. Hawkins. *Acc. Chem. Res.* **1992**, 25, 150–156.
- [2] J. M. Hawkins, S. Loren, A. Meyer, R. Nunlist. *J. Am. Chem. Soc.* **1991**, 113, 7770–7771.
- [3] A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt, R. C. King. *J. Am. Chem. Soc.* **1995**, 117, 5492–5502.
- [4] A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. C. King. *J. Am. Chem. Soc.* **1993**, 115, 5829–5830.
- [5] T. Suzuki, Q. Li, K. C. Khemani, F. Wudl. *J. Am. Chem. Soc.* **1992**, 114, 7301–7302.
- [6] G. A. Burley, P. A. Keller, S. G. Pyne, G. E. Ball. *Chem. Commun.* **2000**, 1717–1718. <http://pubs.rsc.org/en/journals/>
- [7] G. A. Burley, P. A. Keller, S. G. Pyne, G. E. Ball. *J. Org. Chem.* **2002**, 67, 8316–8330.
- [8] G. E. Ball, G. A. Burley, L. Chaker, B. C. Hawkins, J. R. Williams, P. A. Keller, S. G. Pyne. *J. Org. Chem.* **2005**, 70, 8572–8574.
- [9] T. Akasaka, Y. Maeda, T. Wakahara, T. Mizushima, W. Ando, M. Walchli, T. Suzuki, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira, M. Fujitsuka, O. Ito, Y. Sasaki, K. Yamamoto, T. Erata. *Org. Lett.* **2000**, 2, 2671–2674.
- [10] W. T. Ford, T. Nishioka, F. Qiu. *J. Org. Chem.* **2000**, 65, 5780–5784.
- [11] G. A. Burley, P. A. Keller, S. G. Pyne, G. E. Ball. *Magn. Reson. Chem.* **2001**, 39, 466–470.
- [12] M. S. Meier, H. P. Spielmann, R. G. Bergosh, R. C. Haddon. *J. Am. Chem. Soc.* **2002**, 124, 8090–8094.
- [13] M. S. Meier, H. P. Spielmann, R. G. Bergosh, M. C. Tetreau. *J. Org. Chem.* **2003**, 68, 7867–7870.
- [14] G. Sun, M. Kertesz. *New J. Chem.* **2000**, 24, 741–743.
- [15] F. Hauke, Z.-F. Chen, A. Hirsch. *Polish J. Chem.* **2007**, 81, 971–983.
- [16] E. E. Fileti, R. Rivelino. *Chem. Phys. Lett.* **2009**, 467, 339–343.
- [17] L. M. Khalilov, A. R. Tulyabaev, V. M. Yanybin, A. R. Tuktarov. *Magn. Reson. Chem.* **2011**, 49, 378–384.
- [18] L. M. Khalilov, A. R. Tulyabaev, A. R. Tuktarov. *Magn. Reson. Chem.* **2011**, 49, 768–774.
- [19] A. R. Tuktarov, A. R. Akhmetov, V. V. Korolev, A. A. Khuzin, L. L. Khasanova, N. R. Popod'ko, L. M. Khalilov. *Arkivoc* **2011**, 2011, 54–66.
- [20] A. R. Tuktarov, A. A. Khuzin, V. V. Korolev, U. M. Dzhemilev. *Russ. J. Org. Chem.* **2012**, 48, 99–103.
- [21] E. Y. Pankratyev, A. R. Tulyabaev, L. M. Khalilov. *J. Comput. Chem.* **2011**, 32, 1993–1997.
- [22] A. R. Tulyabaev, L. M. Khalilov. *Comput. Theor. Chem.* **2011**, 976, 12–18.
- [23] W. B. Jennings. *Chem. Rev.* **1975**, 75, 307–322.
- [24] G. M. Whitesides, D. Holtz, J. D. Roberts. *J. Am. Chem. Soc.* **1964**, 86, 2628–2634.
- [25] K. Mislow, J. Siegel. *J. Am. Chem. Soc.* **1984**, 106, 3319–3328.
- [26] J. Reisse, R. Ottinger, P. Bickart, K. Mislow. *J. Am. Chem. Soc.* **1978**, 100, 911–915.
- [27] G. A. Morris, R. Freeman. *J. Am. Chem. Soc.* **1978**, 100, 6763–6764.
- [28] E. L. Eliel, S. H. Wilen, M. P. Doyle. *Basic Organic Stereochemistry*, John-Wiley & Sons, Inc., New York, **2001**.

- [29] G. C. Levy, R. L. Lichter, G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy* (2nd edn), John Wiley & Sons, Inc., New York, **1980**.
- [30] J. P. Perdew, K. Burke, M. Ernzerhof. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.
- [31] D. N. Laikov. *Chem. Phys. Lett.* **1997**, 281, 151–156.
- [32] D. N. Laikov, Y. A. Ustynyuk. *Russ. Chem. Bull., Int. Ed.* **2005**, 54, 820–826.
- [33] D. N. Laikov, *The development of an economic approach to calculate molecules by means of Density Functional Theory and its implementation to solve the complex chemical researches*, Ph.D. Dissertation, Moscow State University, **2000**.
- [34] S. K. Wolff, T. Ziegler. *J. Chem. Phys.* **1998**, 109, 895–905.
- [35] T. Heine, G. Seifert, P. W. Fowler, F. Zerbetto. *J. Phys. Chem. A* **1999**, 103, 8738–8746.
- [36] W. H. Powell, F. Cozzi, G. P. Moss, C. Thilgen, R. J.-R. Hwu, A. Yerin. *Pure Appl. Chem.* **2002**, 74, 629–695.

Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's website.