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Endohedral chemical shifts in higher fullerenes with 72–86 carbon atoms

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Abstract. For all isolated pentagon isomers of the fullerenes C_{60}–C_{86} with nonzero HOMO–LUMO gap and for one nonclassical C_{72} isomer (C_{2v}), endohedral chemical shifts have been computed at the GIAO-SCF/3-21G level using B3LYP/6-31G* optimized structures. The experimental ^{3}He NMR signals are reproduced reasonably well in cases where assignments are unambiguous (e.g. C_{60}, C_{70} and C_{76}). On the basis of the calculated thermodynamic stability order and the comparison between the computed and experimental ^{3}He chemical shifts, the assignments of the observed ^{3}He NMR spectra are discussed for all higher fullerenes, and new assignments are proposed for one C_{82} and one C_{86} isomer (C_{82}:3 and C_{86}:17). The calculated helium chemical shifts also suggest the reassignment of the $\delta(^3\text{He})$ resonances of two C_{78} isomers.

Key words: Higher fullerenes – Thermodynamic stability – Endohedral helium chemical shifts

1 Introduction

The interplay between theory and experiment has contributed much to the fast development of fullerene chemistry in the last decade [1]. According to the isolated pentagon rule (IPR), fullerenes generally tend to be more stable when they contain only isolated pentagons. Several IPR isomers of various higher fullerenes have been characterized by identifying the thermodynamically most favorable structures and assigning them to the observed ^{13}C NMR spectra. These include one isomer of C_{70} [2], one isomer of C_{76} [3, 4], three isomers of C_{78} [5–9], two isomers of C_{80} [10, 11] and at least ten isomers of C_{84} [12–17].

Among the other higher fullerenes studied here, the previously called "missing fullerenes" C_{72} and C_{74} have been obtained in reduced form [18–20], and C_{74} has recently been produced in high yield in an arc periphery plasma [21]. Three of the nine IPR isomers of C_{82} exist [6], and the isolation of C_{86} [7] as well as its UV–vis spectrum have been described [22]; however, the isomeric composition of these higher fullerenes is not yet established. Even for C_{72} and C_{74}, which have only one IPR isomer each, a definite characterization has not been given. Some theoretical calculations suggest that C_{72} which is present in the fullerene soot does not satisfy the isolated pentagon rule [23].

Endohedral ^{3}He NMR chemical shifts have proven to be a useful tool for characterizing fullerenes and their derivatives, i.e., different fullerenes with an encapsulated ^{3}He nucleus have very distinct ^{3}He NMR chemical shifts [24]. Moreover, experimental endohedral ^{3}He chemical shifts have been reproduced well by using quantum chemical methods [25–27]; however, a number of ^{3}He NMR spectra for higher fullerenes still remain unassigned, including those reported recently for C_{82} and C_{86} [17]. This gave us the impetus to calculate the endohedral chemical shifts of fullerenes C_{72}–C_{86} in a systematic manner at a uniform theoretical level.

2 Computational details

The geometries of the IPR isomers with nonzero HOMO–LUMO gap of fullerenes C_{72}–C_{86} [28] listed in Table 1 were fully optimized in the given symmetry at the density functional B3LYP/6-31G* level, and were previously employed in Ref. [29]. The nucleus-independent chemical shifts (NICS) [30] at the cage centers, which have essentially the same values as the endohedral helium chemical shifts, were computed at the GIAO-SCF/3-21G level with the B3LYP/6-31G* geometries. The results for C_{60} and C_{70} are also reported for comparison. All these calculations were carried out with the GAUSSIAN 98 suite of programs [31].

3 Results and discussion

The endohedral chemical shifts are summarized in Table 1. The level of the chemical shift computations,

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Table 1. B3LYP/6-31G* energy data (*TE*: total energy; *RTE*: relative total energy) and endohedral chemical shifts (GIAO-SCF/3-21G//B3LYP/6-31G*)

Fullerene	Isomer (symmetry)	TE (au)	RTE (kcal/mol)	Gap (eV)	Nucleus-independent chemical shift[a]	Experimental endohedral ^{3}He NMR	Nucleus-independent chemical shift[b]
C_{60}	1 (I_h)	−2,286.1736	–	2.77	−8.0	−6.3[c]	−8.5
C_{70}	1 (D_{5h})	−2,667.3034	–	2.68	−23.1	−28.8[c]	−31.1
C_{72}	1 (D_{6d})	−2,743.4672	11.5	2.50	−15.7	–	
C_{72}^{2-}	1 (D_{6d})	−2,743.5250	–	1.46	−31.0	–	
C_{72}	C_{2v}	−2,743.4856	0.0	1.47	−22.9	–	
C_{74}	1 (D_{3h})	−2,819.7221	–	0.69	−21.9	–	
C_{74}^{2-}	1 (D_{3h})	−2,819.8364	–	1.60	−19.2	–	
C_{76}	1 (D_2)	−2,895.9534	–	1.98	−16.4	−18.7[d]	−15.0
C_{78}	1 (D_3)	−2,972.1705	9.9	1.62	−11.7	−11.9[d]–17.6[e]	−18.7
C_{78}	2 (C_{2v})	−2,972.1759	6.6	2.02	−15.2	−16.9[d]–16.9[e]	−19.1
C_{78}	3 (C_{2v})	−2,972.1864	0.0	1.65	−15.2	−16.8[d]–11.9[e]	−17.8
C_{78}	4 (D_{3h})	−2,972.1472	24.6	2.47	−14.3	–	−18.5
C_{78}	5 (D_{3h})	−2,972.1792	4.5	1.54	−14.6	–	
C_{80}	1 (D_{5d})	−3,048.3860	2.6	0.98	−2.5	–	
C_{80}	2 (D_2)	−3,048.3901	0.0	1.35	−8.8	–	
C_{80}	3 (C_{2v})	−3,048.3795	6.7	0.80	−7.1	–	
C_{80}	4 (D_3)	−3,048.3759	8.9	0.74	−13.7	–	
C_{80}	5 (C_{2v})	−3,048.3768	8.4	0.67	−1.5	–	
C_{82}	1 (C_2)	−3,124.6235	7.8	1.25	−7.1	–	
C_{82}	2 (C_s)	−3,124.6252	6.7	1.64	−11.2	–	
C_{82}	3 (C_2)	−3,124.6359	0.0	1.56	−10.6	−13.05[e]	
C_{82}	4 (C_s)	−3,124.6297	3.9	1.56	−10.3	–	
C_{82}	5 (C_2)	−3,124.6227	8.3	1.29	−7.5	–	
C_{82}	6 (C_s)	−3,124.6164	12.2	1.11	−3.6	–	
C_{82}	8 (C_{3v})	−3,124.5869	30.8	0.75	48.3	–	
C_{82}	9 (C_{2v})	−3,124.6067	18.3	0.75	6.2	–	
C_{84}	1 (D_2)	−3,200.7979	51.8	2.37	−16.3	–	
C_{84}	2 (C_2)	−3,200.8274	33.3	1.95	−16.8	–	
C_{84}	3 (C_s)	−3,200.8290	32.3	0.79	−6.9		
C_{84}	4 (D_{2d})	−3,200.8565	15.0	2.14	−20.5	−24.35[d]	−25.0
C_{84}	5 (D_2)	−3,200.8548	16.1	1.91	−16.6	–	
C_{84}	6 (C_{2v})	−3,200.8527	17.4	1.37	−8.6	–	
C_{84}	7 (C_{2v})	−3,200.8409	24.8	1.31	−6.2	–	
C_{84}	8 (C_2)	−3,200.8450	22.2	0.99	−8.8	–	
C_{84}	9 (C_2)	−3,200.8382	26.5	0.81	−2.2	–	
C_{84}	10 (C_s)	−3,200.8346	28.7	0.66	−4.4	–	
C_{84}	11 (C_2)	−3,200.8670	8.4	1.64	−9.0	–	
C_{84}	12 (C_1)	−3,200.8606	12.4	1.46	−7.5	–	
C_{84}	13 (C_2)	−3,200.8408	24.9	1.17	−3.0	–	
C_{84}	14 (C_s)	−3,200.8561	15.3	1.91	−11.6	–	
C_{84}	15 (C_s)	−3,200.8622	11.4	1.55	−9.3	–	
C_{84}	16 (C_s)	−3,200.8675	8.1	1.78	−10.0	–	
C_{84}	17 (C_{2v})	−3,200.8457	21.8	1.37	−6.4	–	
C_{84}	18 (C_{2v})	−3,200.8552	15.8	1.96	−10.8	–	
C_{84}	19 (D_{3d})	−3,200.8639	10.4	1.38	−6.9	–	−9.4
C_{84}	20 (T_d)	−3,200.8313	30.8	2.65	−12.6	–	−15.3
C_{84}	21 (D_2)	−3,200.8543	16.4	1.35	−6.4	–	
C_{84}	22 (D_2)	−3,200.8798	0.4	1.98	−9.6	−8.96[d]	−12.4
C_{84}	23 (D_{2d})	−3,200.8804	0.0	2.06	−9.5	–	−11.9
C_{84}	24 (D_{6h})	−3,200.8689	7.2	2.34	−11.7	–	−14.8
C_{86}	1 (C_1)	−3,277.0468	26.2	1.14	−19.3	–	
C_{86}	2 (C_2)	−3,277.0452	27.2	2.12	−20.9	–	
C_{86}	3 (C_2)	−3,277.0590	18.6	1.17	−18.6	–	
C_{86}	4 (C_2)	−3,277.0546	21.3	0.88	−8.3	–	
C_{86}	5 (C_1)	−3,277.0563	20.3	1.01	−12.4	–	
C_{86}	6 (C_2)	−3,277.0642	15.3	0.97	−12.9	–	
C_{86}	7 (C_1)	−3,277.0498	24.4	0.87	−0.8	–	
C_{86}	8 (C_s)	−3,277.0333	34.7	0.85	6.1	–	
C_{86}	9 (C_{2v})	−3,277.0236	40.8	0.81	24.8	–	
C_{86}	10 (C_{2v})	−3,277.0598	18.1	1.07	−16.6	–	
C_{86}	11 (C_1)	−3,277.0720	10.4	1.15	−9.6	–	

Table 1. (Contd.)

Fullerene	Isomer (symmetry)	TE (au)	RTE (kcal/mol)	Gap (eV)	Nucleus-independent chemical shift[a]	Experimental endohedral ^{3}He NMR	Nucleus-independent chemical shift[b]
C_{86}	12(C_1)	−3,277.0722	10.3	1.19	−10.3	–	
C_{86}	13 (C_1)	−3,277.0657	14.4	1.20	−8.2	–	
C_{86}	14 (C_2)	−3,277.0544	21.5	0.98	−7.0	–	
C_{86}	15 (C_s)	−3,277.0535	22.0	1.06	−7.7	–	
C_{86}	16 (C_s)	−3,277.0787	6.2	1.88	−13.8	–	
C_{86}	17 (C_2)	−3,277.0886	0.0	1.54	−10.9	−10.58[e]	
C_{86}	18 (C_3)	−3,277.0706	11.3	1.14	−17.0	–	
C_{86}	19 (D_3)	−3,277.0509	23.7	1.00	−7.5	–	

[a] This work

[b] GIAO-SCF/DZP//MP2/TZP level for C_{60} and C_{70}, GIAO-SCF/DZP//BP86/3-21G level for C_{76}, C_{78} and C_{84}, from Refs. [27, 33]. For endohedral chemical shifts of C_{60} and C_{70} at other levels of theory see Ref. [33]

[c] $\delta(^3He)$ from Ref. [32]

[d] $\delta(^3He)$ from Ref. [16]

[e] $\delta(^3He)$ from Ref. [17]

GIAO-SCF/3-21G, is not sufficient for quantitative predictions. For instance, a relatively large deviation from experiment (exceeding 5 ppm) is found for He@C_{70} [32]. According to the experience accumulated so far, the theoretical $\delta(^3He)$ values tend to agree better with available experiments upon increase of the basis set size and inclusion of electron correlation [27, 33, 34]. Nevertheless, the chosen level should be sufficient to capture qualitative trends between individual isomers. In the following, some of these trends are discussed.

The IPR isomer of C_{72} with D_{6d} symmetry is predicted to have very high chemical stability because of its large HOMO–LUMO gap, which is comparable with that of C_{60} and C_{70}. On the other hand, the IPR isomer C_{74} (D_{3h}) is of high chemical reactivity because of its unusually small HOMO–LUMO gap [35], which may explain its absence in the normal fullerene solvent extraction from primary soot. Recently the small gap energy of C_{74} has been confirmed experimentally [20, 36]. The dianions C_{72}^{2-} and C_{74}^{2-}, which have been observed experimentally [18–20], both have significant gap energies. Upon reduction to the dianions, the encapsulated helium atom in C_{72} becomes much more shielded (-31.0 ppm versus −15.7 ppm in the neutral), while there is a slight deshielding for He@C_{74} (−19.2 ppm in the dianion versus −21.9 ppm in the neutral).[1] The non-IPR isomer C_{72} (C_{2v}) has been predicted to be more stable than the IPR isomer C_{72} (D_{6d}) at the B3LYP/6-31G//RHF/3-21G level [23]. This is confirmed at the B3LYP/6-31G* level: C_{72} (C_{2v}) is 11.5 kcal/mol more stable than C_{72} (D_{6d}) and also more aromatic according to the NICS value of −22.9 ppm.

Only the D_2 isomer of C_{76}, which is one of the two mathematically possible IPR structures (the other is of T_d symmetry and has a vanishing HOMO–LUMO gap [28]), has been extracted from the fullerene soot and characterized. The computed endohedral helium chemical shift of He@C_{76} is −16.4 ppm, close to the experimental value of −18.7 ppm [16].

Among the five IPR structures of C_{78}, three isomers (D_3, C_{2v} and C_{2v}') have been isolated and characterized. C_{78}:3, with C_{2v} symmetry, is the lowest-energy isomer, but the least abundant one as observed experimentally [7]. In 1995, the endohedral chemical shifts of C_{78} were reported by Saunders et al. [16], and three ^{3}He NMR signals were assigned to the isolated isomers while two ^{3}He NMR signals remained unassigned. The assumption that the five signals ascribed to C_{78} could be due to the five possible IPR isomers [33] was later refuted since two of these resonances were identified as being due to doubly labeled species [17].

Our calculated NICS values support the assignment of the other three ^{3}He NMR signals to IPR isomers (−11.9 ppm D_3, −16.9/−16.8 ppm C_{2v} and C_{2v}') [16]; however, the assignment of the signal at −11.9 ppm has been changed to isomer C_{2v}' more recently, without providing new supporting evidence [17]. Clearly the accord between theoretical and experimental endohedral shifts would be improved if the original assignment of the C_{2v}' and D_3 isomers [17] were retained.

There are seven distinct possible molecular geometries of C_{80} which satisfy the IPR, namely I_h, D_{5d}, D_{5h}, D_3, D_2, C_{2v} and C_{2v}'. Among these, D_{5h} and I_h have a zero HOMO–LUMO gap [28] and will not be studied here. It was not until 1996 that a small quantity of the D_2 isomer was isolated [10] and characterized [37] and not until 2000 that the D_{5d} isomer was isolated [11]. On the theoretical side, the D_{5d} and D_2 structures were computed to be the lowest-energy isomers at different levels [11, 38–41]. Our B3LYP/6-31G* calculations agree with these literature results. The computed encapsulated helium chemical shifts for the D_2 and D_{5d} isomers are −8.8 and −2.5 ppm, respectively.

There are nine IPR isomers for C_{82}, eight of which show a nonzero HOMO–LUMO gap [28]. C_{82} was observed experimentally as a lanthanum-doped form, La@C_{82}, as early as 1991 [42], and until recently the cage

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[1] For highly charged anions (hexaanions), chemical shifts from density functional theory have proven superior to self-consistent-field values [27, 34]; for $\delta(^3He)$ of He@C_{72}^{2-} and He@C_{74}^{2-}, values of −25.7 and −17.9 ppm, respectively, are computed at the GIAO-B3LYP/6-31G* level, i.e., qualitatively similar to the GIAO-SCF/3-21G data.

structure of this doped species was interpreted to have C_{2v} symmetry [43, 44]. The bare C_{82} cluster was isolated by Tagmatarchis et al. [13] and Dennis et al. [14] and also was observed by Wang et al. [17], but a detailed characterization for the bare cluster has not been achieved so far. According to the ^{13}C NMR spectra, three isomers of C_{82} were identified to be of C_2 symmetry [6]. Our calculations indicate that one of the three C_2 isomers is the lowest-energy structure, and its endohedral helium chemical shift is computed to be −10.6 ppm, close to the experimental value of one He@C_{82} isomer, −13.0 ppm [17]. Thus, the C_{82} isomer observed in the experiment of Wang et al. [17] may be assigned to C_{82}:3 on the basis of the order of stability and the agreement between the computed and experimentally observed encapsulated helium chemical shifts. The other two C_2 isomers detected by ^{13}C NMR [6], C_{82}:1 and C_{82}:5, are also calculated to be relatively stable, about 8 kcal/mol above C_{82}:3, and their endohedral chemical shifts are predicted to be −7.1 and −7.5 ppm, respectively. It should also be noted that two C_s isomers, C_{82}:2 and C_{82}:4, fall in the energy range of the three observed C_2 isomers. Since they also have considerable gap energies, they might be synthesized eventually.

Considerable effort has been taken to isolate and characterize C_{84} isomers. There are 24 structural isomers of C_{84} that obey the IPR [28]. Two main isomers, D_2 (C_{84}:22) and D_{2d} (C_{84}:23) [12], and four minor isomers, D_{6h} (C_{84}:24) and D_{3d} (C_{84}: 19) [13], D_{2d} (C_{84}:4) and D_2 (C_{84}:5) [14], have been isolated and characterized by their ^{13}C NMR spectra. Other isomers have also been observed experimentally, including two C_2 [13], two C_s and one of unassigned symmetry [14]. Thus, up to now, at least ten isomers (eight reported in Ref. [14] and two reported in Ref. [13]) have been isolated so far.

Since the existence of several isomers with the same symmetry prevents the unambiguous identification solely from the number and intensity of the ^{13}C NMR peaks, the computed energy order was used to assist in the identification of the C_{84} isomers. In this way, two of the five mathematically possible C_s isomers have been assigned to C_{84}:15 and C_{84}:16 [15] and one of the five possible C_2 isomers to C_{84}:11 [13, 15]. These assignments are consolidated by our calculations since they are the lowest-energy isomers among the structures of the given symmetry. The other C_2 isomer detected by Tagmatarchis et al. [13] might be the second most stable C_2 isomer, C_{84}:8, according to our calculations. Concerning the minor D_2 isomers, one of them was assigned to C_{84}: 21 by combining the computed energy order (at the MNDO level) and the ^{13}C NMR spectra [15]. Our calculations at the B3LYP/6-31G* level indicate that C_{84}:21 and C_{84}:5 are nearly isoenergetic, with C_{84}:5 being preferred by 0.3 kcal/mol and showing a bigger HOMO–LUMO gap. It is thus unclear which of these two D_2 isomers may have been present in the experiment [15].

In 1995, Saunders et al. [16] observed nine different C_{84} isomers in the ^{3}He NMR spectrum and assigned the signal at −8.96 ppm to the main isomer, C_{84}:22, which is supported by our calculations, while other signals remained unidentified. However, since some of the ^{3}He signals were recognized as those of doubly labeled isomers, the ^{3}He NMR spectra are now interpreted in terms of seven different isomers. The ^{3}He NMR spectra for these seven isomers range between −7.5 and −14.1 ppm, but these isomers still cannot be assigned unambiguously [17]. One exception is C_{84}:4, whose computed endohedral chemical shift is far outside the range covered by other isomers [37] and can be assigned accordingly.

Overall the computed ^{3}He NMR spectra have only limited value for assigning the C_{84} isomers. As pointed out before [27], since most of the helium NMR signals cover a chemical-shift range comparable to, or smaller than, the variations of the ab initio results, assignments are difficult where several isomers are present. However, if specific isomers can be isolated, the ^{3}He NMR spectra can be helpful to distinguish between isomers with the same symmetry whenever the ^{13}C NMR spectra are not sufficient for a straightforward characterization.

C_{86} has received less attention both from experiment and theory. The density functional results for all 19 IPR isomers of C_{86} are listed in Table 1. The most stable isomer is C_{86}:17, with C_2 symmetry, followed by C_{86}:16, with C_s symmetry. Recently Wang et al. [17] reported the helium NMR signal (−10.58 ppm) of one C_{86} isomer. This agrees very well with our calculated helium chemical shift, −10.9 ppm, for the most stable isomer, C_{86}:17. Thus, the observed isomer [17] may be assigned to be C_{86}:17 on the basis of the thermodynamic stability and the helium chemical shift.

In conclusion, all IPR structures with nonzero HOMO–LUMO gap of fullerenes C_{60}–C_{86} as well as one nonclassical stable isomer of C_{72} (C_{2v}) have been optimized at B3LYP/6-31G* level, and their encapsulated helium chemical shifts have been computed at the GIAO-SCF/3-21G level. The experimental ^{3}He NMR signals of C_{60}, C_{70}, C_{76} and two isomers of C_{84} are reproduced reasonably well. On the basis of the calculated thermodynamic stability order and the comparison between the computed and experimental ^{3}He chemical shifts, we propose assignments for one C_{82} and one C_{86} isomer (C_{82}:3 and C_{86}:17), respectively. The calculated helium chemical shifts of C_{78} isomers support the original assignment of the isomeric composition by Saunders et al. [16] in 1995 and suggest a revision of the recent reassignment of some isomers [17]. The computed helium NMR signals may sometimes only be of limited value for assignment purposes, for example, for C_{84}, where many signals appear in a narrow range. Nevertheless, even in such cases, the computations can still help to characterize isolated isomers with a given symmetry. The differences in the theoretical helium chemical shifts between different isomers in conjunction with the predicted thermodynamic stability order will continue to facilitate the identification of the isomers of higher fullerenes in the future.

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