

Theoretical NMR ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ Scalar Couplings as Probes to Study Diamagnetic Ring Currents in Fullerenes

Rubén H. Contreras,¹ Juan E. Peralta,² Verónica Barone²
and Gustavo E. Scuseria²

¹*Department of Physics, FCEyN, University of Buenos Aires and CONICET, Buenos Aires, Argentina*

²*Department of Chemistry, Rice University, Houston, TX 77005-1892, USA*

Abstract

In this work $J({}^{13}\text{C}, {}^{13}\text{C})$ coupling constants and the principal components of nuclear magnetic shielding constants in the C_{60} , C_{70} , and $\text{C}_{60}^{(6-)}$ fullerenes are calculated at the B3LYP/cc-pCVDZ-sd level using optimized B3LYP/cc-pCVDZ geometries. Indirect spin–spin couplings are utilized to study local diamagnetic ring currents in fullerenes. In unsaturated carbon containing compounds, the Fermi contact (FC) contribution to long-range ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ ($n > 4$) coupling constants is mainly transmitted through the mobile π -electronic system following a few simple rules: the alternating sign-rule and the pathway invariance. Besides, the absolute value of such a coupling decreases slowly when increasing the number of bonds separating the coupled nuclei. Without explicitly addressing the controversial topic of the aromaticity of fullerenes, we show that the π -transmitted components of the FC contribution provide information on factors affecting ring currents in fullerenes.

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1. INTRODUCTION

High resolution NMR parameters are recognized as invaluable probes to detect fine details of the electronic molecular structure of different types of compounds when adequate combinations of theoretical and experimental approaches are adopted. Pioneer works of Professor Oddershede on the study of high resolution NMR parameters are very well recognized in the literature [1–6]. For this reason and for this occasion, the authors thought it pertinent to present a contribution

where calculated coupling constants are useful to study the behavior of diamagnetic ring currents in fullerenes.

Since the discovery of the C_{60} fullerene [7], the existence of ring current contributions to the magnetic susceptibility in this compound has been a rather controversial issue [8]. Smalley and co-workers [7] suggested that C_{60} is a spheroidal aromatic molecule and supported this assumption with π -electron and total energy calculations. On the other hand, the computation [8] of the π -electron ring-current susceptibility of C_{60} using the finite-field version of the original London theory [9] suggested that this is an aromatic molecule with vanishingly small ring current susceptibility. Fowler *et al.* [10] performed the first *ab initio* calculation on the polarizability and magnetizability of C_{60} and they predicted a C_{60} net diamagnetism as well as diamagnetic effects on the NMR chemical shift of an encapsulated atom. Commenting critically on the Fowler *et al.* paper, Haddon and Elser [11] argued that the magnetic susceptibility of C_{60} is incompatible with its description as a normal aromatic molecule. This controversy arose a renewed interest for quantifying the ‘aromaticity’ of a conjugated aromatic compound and several new criteria were established to quantify such a property. Among them, the following are worth mentioning: the ‘nucleus-independent chemical shift’ [12,13], the ‘harmonic oscillator model of aromaticity’ index [14], the ‘para-delocalization index’ [15], and the ‘ring-current analysis’ [16]. In a detailed review, Lazzeretti [17] gives an account of different magnetic criteria for aromaticity.

Spin–spin coupling constants, when properly analyzed, can provide insight into the fine details of the electronic molecular structure [18,19]. However, a good amount of information can frequently be obtained resorting only to some known features of these spectral parameters. In this work, an approach of this type is applied to study diamagnetic ring currents in C_{60} and in C_{70} . Our methodology is based on well-known transmission features of the Fermi contact (FC) contribution to long-range spin–spin couplings in conjugated systems [20].

When comparing the molecular electronic structures of C_{60} and C_{70} , one of the most striking differences is observed when considering the ^3He chemical shifts in endohedral ^3He at C_{60} and ^3He at C_{70} . In fact, ^3He atoms encapsulated in these endohedral compounds appear at, respectively, -6.4 and -28.8 ppm, relative to dissolved ^3He at 0.0 ppm [21,22]. Such differences in the ^3He shielding suggest that even though diamagnetic ring currents are significant in these two fullerene compounds, they are more important for shielding the encapsulated He atom in C_{70} than in C_{60} [23]. Saunders *et al.* [21] consider that C_{70} should be classified as aromatic, while the aromaticity of C_{60} is less well defined.

Several notably different features are observed in the ^{13}C NMR spectra of C_{60} [24] and C_{70} [25,26]. The former consists of only one line, at *ca.* 143 ppm down field from TMS, indicating that the 60 C atoms in C_{60} are all magnetically equivalent in agreement with its icosahedral symmetry. Because of its symmetry and the existence of only one C magnetic isotope, $J(^{13}\text{C}, ^{13}\text{C})$ spin–spin couplings are not amenable to measurement in C_{60} . On the other hand, the ^{13}C NMR spectrum of C_{70} consists of five lines [25], indicating that there are five magnetically non-equivalent ^{13}C nuclei, which is compatible with D_{5h} symmetry [27], and therefore there are only four $^1J(^{13}\text{C}, ^{13}\text{C})$ couplings amenable to

measurement [25]. To the best of the authors' knowledge, ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ with $n > 1$ have not been observed yet for C_{70} . Long-range couplings ($n > 4$) should be interesting probes to study several features of diamagnetic ring currents since they are known to be greatly dominated by the FC term, and they are mainly transmitted through the mobile π -bond systems [28–30]. It is well known that such long-range couplings follow simple rules, like for instance, the alternating sign rule, [i.e., ${}^nJ({}^{13}\text{C}, {}^{13}\text{C}) > 0$ if n is odd and ${}^nJ({}^{13}\text{C}, {}^{13}\text{C}) < 0$ if n is even], the pathway invariance, and the low sensitivity of its absolute value with n . For this reason, it is expected that such couplings provide valuable information on diamagnetic ring currents. As experimental ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ ($n > 1$) have not yet been reported on fullerenes, theoretically calculated couplings supply helpful information, provided they are obtained at a high level of theory. Such a high level can be achieved with the DFT formalism if both adequate functional and basis set are used [31]. In a previous paper from our group, excellent agreement was reported between DFT-B3LYP/cc-pCVDZ-sd calculated [32] and experimental [25] ${}^1J({}^{13}\text{C}, {}^{13}\text{C})$ spin–spin coupling constants for C_{70} . This suggests that this level of theory is also adequate for calculating ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ ($n > 4$) couplings in C_{60} , C_{70} , and $\text{C}_{60}^{(6-)}$. It is important to stress that calculated ${}^1J({}^{13}\text{C}, {}^{13}\text{C})$ couplings [32] were not only in excellent agreement with the experimental values, but they also provided an interesting rationalization of some aspects of the C_{70} diamagnetic ring currents along the borders of the belt [32]. This rationalization was found to be compatible with the experimental trends of its ${}^{13}\text{C}$ chemical shifts. The excellent agreement between calculated and measured ${}^1J({}^{13}\text{C}, {}^{13}\text{C})$ couplings in C_{70} supports the idea of relying on C_{60} calculated $J({}^{13}\text{C}, {}^{13}\text{C})$ couplings to obtain insight into C_{60} diamagnetic currents. Both one-bond as well as long-range $J({}^{13}\text{C}, {}^{13}\text{C})$ couplings are expected to be adequate probes for such study. Since the London theory predicts that the $\text{C}_{60}^{(6-)}$ anion is strongly diamagnetic because diamagnetic ring currents flow around its hexagons as well as its pentagons [8,33–36], ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ spin–spin couplings in the anion are also calculated at the same level of theory in this work.

2. COMPUTATIONAL DETAILS

All calculations carried out in this work were performed with the Gaussian 03 [37] suite of programs. The geometries of C_{60} and $\text{C}_{60}^{(6-)}$ were optimized at the B3LYP/cc-pVDZ level assuming icosahedral symmetry. In both compounds, all four terms of isotropic ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ coupling constants, namely, FC, spin-dipolar (SD), paramagnetic spin-orbital (PSO), and diamagnetic spin-orbital (DSO), were calculated at the B3LYP/cc-pCVDZ-sd level. The cc-pCVDZ-sd basis set is cc-pCVDZ [38] with all s functions fully decontracted. Isotropic and anisotropic nuclear magnetic shielding constants in C_{60} , $\text{C}_{60}^{(6-)}$, and C_{70} were calculated using the gauge-included atomic orbitals (GIAO) approach [39,40] at the same level of theory employed for the spin–spin couplings. For comparison, ${}^nJ({}^{13}\text{C}, {}^{13}\text{C})$ spin–spin couplings and the ${}^{13}\text{C}$ magnetic shielding tensor in benzene were also calculated using the cc-pCVDZ-sd basis set for C atoms and the

totally decontracted cc-pVDZ basis set for H atoms (its geometry was optimized at the same level).

3. RESULTS AND DISCUSSION

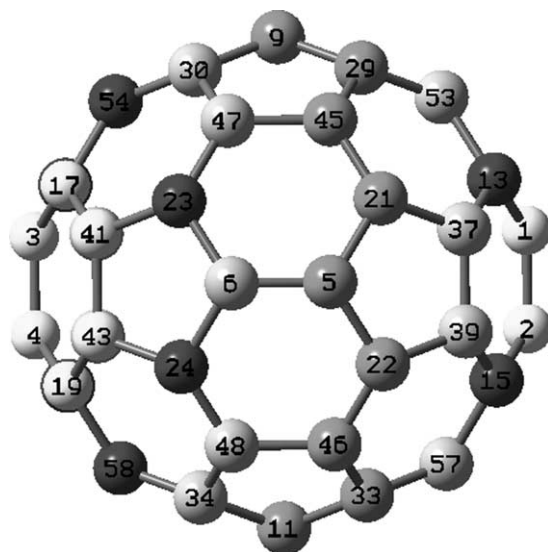
The calculated four isotropic contributions to the two different $^1J(^{13}\text{C}, ^{13}\text{C})$ spin–spin coupling constants in C_{60} are compared in Table 1 with the analogous contributions to $^1J(^{13}\text{C}, ^{13}\text{C})$ couplings in $\text{C}_{60}^{(6-)}$ and in C_{70} reported recently [32]. The numbering of carbon nuclei in C_{60} and $\text{C}_{60}^{(6-)}$ and in C_{70} is displayed in Schemes 1 and 2, respectively. Couplings in all these three compounds were calculated at the same level of theory. In the same Table 1, isotropic contributions to the calculated $^1J(^{13}\text{C}, ^{13}\text{C})$ coupling in benzene are also displayed and its total value is compared with the corresponding experimental value [41]. The two different $^1J(^{13}\text{C}, ^{13}\text{C})$ couplings in C_{60} correspond to a side shared by a pentagon ring and an hexagon ring ($J_a = 55.3$ Hz, bond length $B_a = 1.456$ Å, according to the optimized geometry), and to a side shared by two hexagon rings ($J_b = 68.5$ Hz, bond length $B_b = 1.397$ Å), respectively. Each hexagon ring contains three bonds of type B_b alternated with three bonds of type B_a . The FC, SD and PSO contributions to J_a and J_b are typical of a conjugating C–C bond sequence [42], and therefore π -electron delocalization along a sequence of type $-B_a-B_b-B_a-B_b-$ can be expected. Such an electron delocalization corresponds to a diamagnetic current and it represents an efficient pathway for transmitting the π -component of the FC contribution to long-range couplings. On the other hand, all pentagon rings are equilateral in C_{60} , and therefore, the above rationalization suggests that there are no diamagnetic currents along a pentagon, in agreement with assumptions commonly found in

Table 1. Different isotropic contributions to calculated $^1J(^{13}\text{C}, ^{13}\text{C})$ spin–spin couplings (Hz) in C_{60} , C_{70} and $\text{C}_{60}^{(6-)}$. They are compared with the corresponding values in benzene

Comp.	$^1J(\text{C}_i, \text{C}_j)$	FC	SD	PSO	DSO	Total
C_{60}	$^1J(\text{C}_1, \text{C}_2)$	73.6	1.6	−7.2	0.4	68.5
	$^1J(\text{C}_1, \text{C}_{13})$	58.8	0.7	−4.6	0.4	55.3
C_{70}	$^1J(\text{C}_1, \text{C}_2)$	58.5	0.7	−4.7	0.4	54.9
	$^1J(\text{C}_1, \text{C}_{11})$	73.6	1.5	−7.1	0.4	68.4 ^a
	$^1J(\text{C}_{11}, \text{C}_{36})$	58.6	0.7	−4.7	0.4	55.0 ^a
	$^1J(\text{C}_{36}, \text{C}_{22})$	70.9	1.5	−7.2	0.4	65.7
	$^1J(\text{C}_{36}, \text{C}_{56})$	58.1	0.7	−4.5	0.4	54.7 ^a
	$^1J(\text{C}_{56}, \text{C}_{41})$	64.0	1.1	−5.9	0.4	59.7
	$^1J(\text{C}_{56}, \text{C}_{66})$	65.7	1.0	−6.0	0.4	61.1 ^a
	$^1J(\text{C}_{66}, \text{C}_{62})$	59.7	0.6	−4.5	0.4	56.3
$\text{C}_{60}^{(6-)}$	$^1J(\text{C}_1, \text{C}_2)$	62.5	0.3	−5.2	0.4	58.0
	$^1J(\text{C}_1, \text{C}_{13})$	57.1	0.8	−5.2	0.4	53.1
C_6H_6		61.5	1.3	−6.7	0.2	56.3 ^b

^a Experimental values: $^1J(\text{C}_1, \text{C}_{11}) = 68$ Hz; $^1J(\text{C}_{11}, \text{C}_{36}) = 55$ Hz; $^1J(\text{C}_{36}, \text{C}_{56}) = 55$ Hz; $^1J(\text{C}_{56}, \text{C}_{66}) = 62$ Hz (taken from Ref. [25]).

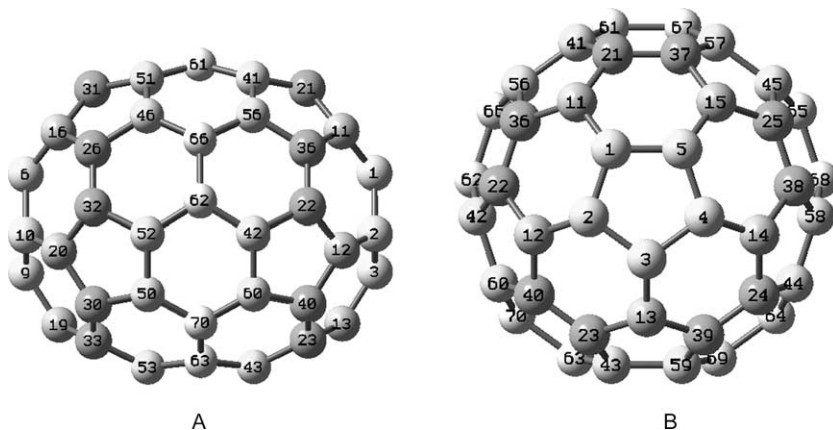
^b Experimental value: 55.87 Hz (taken from Ref. [41]).



Scheme 1.

the literature [33]. The sequence along a C_{60} pentagon ring is $B_a-B_a-B_a-B_a-B_a$, and the corresponding total calculated one-bond coupling is 55.3 Hz.

${}^{13}\text{C}$ magnetic shielding constants for C_{60} , C_{70} , $\text{C}_{60}^{(6-)}$, and benzene are displayed in Table 2. The anisotropy of the corresponding magnetic shielding tensors increases along the fullerene series. It is observed that the calculated anisotropy of the benzene ${}^{13}\text{C}$ magnetic shielding tensor is somewhere between those of C_{60} and C_{70} . The experimental values of the principal components of the C_{60} chemical shift tensor are 220, 186, and 40 ppm [43]. Following Cioslowski [33], the known values of the ${}^{13}\text{C}$ chemical shift in C_{60} and the magnetic shielding constant in benzene can be used to calculate the ‘experimental’ shielding constant in C_{60} at



Scheme 2.

Table 2. GIAO-DFT-B3LYP/cc-pCVDZ-sd ^{13}C magnetic shielding tensors (in ppm) in C_{60} , C_{70} and $\text{C}_{60}^{(6-)}$

		Eigenvalues			Aniso	Iso
C_{60}^{a}		-30.1	0.1	144.6	163.1	39.4
C_{70}^{b}	C_1	-50.5	-15.6	157.1	190.1	30.3
	C_{11}	-40.7	-14.6	159.8	187.5	34.8
	C_{21}	-49.1	-11.7	161.4	191.8	33.5
	C_{41}	-37.9	-17.3	162.8	190.3	35.8
	C_{61}	-23.1	-1.7	177.3	190.3	51.0
$\text{C}_{60}^{(6-)}$		-59.0	-52.3	166.9	222.6	18.5
Benzene		-50.4	45.4	176.3	178.7	57.1

^a Experimental principal values -34; 0 and 146 ppm (see Ref. [33]).

^b Assignments made according to Ref. [25]. The numbering of C atoms is shown in Scheme 2.

43 ppm (39.4 ppm, according to Table 2), as well as the ‘experimental’ values of principal components of the shielding tensor, i.e., -34, 0, and 146 ppm [33] (-30.1, 0.1, and 144.6 ppm, according to Table 2). A few other calculated isotropic magnetic shielding constant for C_{60} found in the literature are 40.43 ppm [44] (HF); 51.3 ppm [45] (IGLO-DFTB), and 50.59 ppm [46] (B3LYP/6-31G**/GIAO-B3LYP/6-31G*).

In Table 3, the calculated chemical shifts in C_{70} are compared with those calculated by Sun and Kertesz [46] and the experimental values given by Taylor *et al.* [26]. Values in Table 3 are referred to C_{60} at 143.15 ppm [47]. The important shielding effect on C_e was attributed mainly to the shielding effect of diamagnetic ring currents circulating through the borders of the belt. Similarly, the important deshielding effect on C_a was attributed to the position of site *a* outside of the belt ring currents. The total shielding span of values shown in Table 3 is 20.70 ppm (this work), 19.17 ppm (Sun and Kertesz) and 19.79 ppm (experimental).

When comparing the magnetic shielding tensors in C_{60} and $\text{C}_{60}^{(6-)}$, it is observed that the six extra electrons in the latter yield an important increase in the anisotropy and a strong shielding effect in the isotropic part of the nuclear shielding.

Table 3. Comparison between calculated and experimental ^{13}C chemical shifts in C_{70} (in ppm) referred to C_{60} at 143.15 ppm (taken from Ref. [47])

C atom ^a	C atom ^b	This work	Ref. ^c	Exp. ^d
C_1	C_a	152.25	151.24	150.54
C_{21}	C_c	149.05	148.23	147.99
C_{11}	C_b	147.75	147.03	147.29
C_{41}	C_d	146.33	146.75	145.66
C_{61}	C_e	131.55	132.07	130.75

^a Numbering of C atoms as in Scheme 2.

^b Labeling of C atoms as in Ref. [25] (*a* to *e* are the distinct sites from cap to belt).

^c Ref. [46].

^d Experimental values taken from Ref. [26].

The potential of long-range couplings as probes to study diamagnetic ring currents is first exemplified considering the ${}^nJ(^{13}\text{C}, ^{13}\text{C})$ couplings in C_{70} . We emphasize that only the π -transmitted component of the FC contribution can provide insight into diamagnetic ring currents. Therefore, only long-range ${}^nJ(^{13}\text{C}, ^{13}\text{C})$ couplings with $n > 4$ are useful for this analysis since those with $n \leq 4$ may have substantial contributions transmitted through the σ -framework and, consequently, the π -contribution could be masked. For instance, if $n = 4$ and the coupled nuclei are connected by a ‘W’ pathway a positive σ -component of a larger absolute value than the respective π -component is expected. Rationalization of ring currents along the belt borders $\text{C}_{41}\text{--}\text{C}_{56}\text{--}\text{C}_{36}\text{--}\text{C}_{22}\text{--}\text{C}_{42}\dots$ and its specular sequence, $\text{C}_{51}\text{--}\text{C}_{46}\text{--}\text{C}_{26}\text{--}\text{C}_{32}\text{--}\text{C}_{52}\dots$ in C_{70} was based on ${}^1J(^{13}\text{C}, ^{13}\text{C})$ couplings [32]. These currents indicate that long-range couplings are efficiently transmitted along such pathways and the corresponding FC contributions are transmitted mainly by the mobile π -electronic system following well-known trends like the alternating sign rule and the pathway invariance [48]. However, when analyzing such couplings in C_{70} as well as in other fullerenes, it should be taken into account that in general, there are several pathways connecting a given pair of C atoms. Each of these pathways is efficient for transmitting the π -component of the FC contribution only if there is a diamagnetic ring current along this pathway. When two carbon atoms are connected by more than one pathway, like for instance some of type n and some of type $n + 1$, there should be a near cancellation of the resulting FC term, unless one of such pathways is not efficient in transmitting a diamagnetic ring current. The sign of the FC term of such coupling should indicate which one is the more efficient pathway. The diamagnetic ring currents along the border belt atoms in C_{70} transmit the FC contribution to long-range couplings along each border. A sequence of FC terms transmitted along the border belt is displayed in Table 4. This sequence is compared with another one involving pathways transversal to the borders of the belt. It is important to note that atoms C_{53} and C_{61} are connected by several pathways with some nine- and eight-bond pathways. Therefore, there is a competition between contributions transmitted through pathways containing odd and even number of bonds (i.e., they are of different ‘parity’). The calculated FC term of ${}^{8,9}J(\text{C}_{53}, \text{C}_{61})$ is $+0.24$ Hz. This suggests that the nine-bond pathways (e.g., $\text{C}_{53}\text{--}\text{C}_{33}\text{--}\text{C}_{30}\text{--}\text{C}_{50}\text{--}\text{C}_{52}\text{--}\text{C}_{32}\text{--}\text{C}_{26}\text{--}\text{C}_{46}\text{--}\text{C}_{51}\text{--}\text{C}_{61}$) are

Table 4. Comparison between the FC term of several long-range ${}^nJ(\text{C}_i, \text{C}_j)$ couplings (in Hz) in C_{70} transmitted along the belt and transversal to it

n		Belt		Transversal
9	$J(\text{C}_{53}, \text{C}_{61})$	+0.24		$J(\text{C}_{10}, \text{C}_1)$ -0.05
8	$J(\text{C}_{63}, \text{C}_{61})$	-0.20		$J(\text{C}_{20}, \text{C}_1)$ +0.04
7	$J(\text{C}_{63}, \text{C}_{41})$	+0.21		$J(\text{C}_{32}, \text{C}_1)$ -0.02
6	$J(\text{C}_{63}, \text{C}_{56})$	-0.24		$J(\text{C}_{52}, \text{C}_1)$ -0.16
5	$J(\text{C}_{63}, \text{C}_{56})$	+0.41		$J(\text{C}_{62}, \text{C}_1)$ +0.26
4	$J(\text{C}_{63}, \text{C}_{22})$	+0.12		$J(\text{C}_{42}, \text{C}_1)$ -0.75
3	$J(\text{C}_{63}, \text{C}_{42})$	+3.14		$J(\text{C}_{22}, \text{C}_1)$ +3.71
2	$J(\text{C}_{63}, \text{C}_{60})$	+1.19		$J(\text{C}_{36}, \text{C}_1)$ +1.29
1	$J(\text{C}_{63}, \text{C}_{70})$	+59.74		$J(\text{C}_{11}, \text{C}_1)$ +73.60

more efficient for transmitting the FC term than the eight-bond pathways (e.g., $C_{53}-C_{33}-C_{30}-C_{20}-C_{32}-C_{26}-C_{46}-C_{51}-C_{61}$). It should be noted that, for symmetry reasons, ${}^1J(C_{30},C_{20}) = {}^1J(C_{20},C_{32}) = 55.0$ Hz (calculated total couplings), and therefore the $C_{30}-C_{20}-C_{32}$ fragment of the eight-bond pathway is not efficient for transmitting the FC term of the ${}^{8,9}J(C_{53},C_{61})$ coupling. On the other hand, the $C_{30}-C_{50}-C_{52}-C_{32}$ fragment of a nine-bond pathway is efficient for transmitting the FC term of ${}^9J(C_{53},C_{61})$ since ${}^1J(C_{30},C_{50}) = 54.7$ Hz; ${}^1J(C_{50},C_{52}) = 59.7$ Hz and ${}^1J(C_{52},C_{32}) = 54.7$ Hz (calculated total couplings), which correspond to a conjugating sequence. Both fragment pathways are part of a pentagon, but only the latter is efficient for transmitting the π -component of the FC contribution to long-range couplings. A similar reasoning holds for the FC contribution to the ${}^{8,9}J(C_{63},C_{61}) = -0.20$ Hz coupling. In this case, the nine-bond pathway involves the $C_{30}-C_{20}-C_{32}$ fragment and therefore, this pathway is not efficient for transmitting the π -component of the FC term. Other couplings transmitted through pathways along the belt ($n > 4$) (shown in Table 4) follow nicely the alternating sign rule. The example shown for $n = 4$, i.e., ${}^4J(C_{63},C_{22}) = +0.12$ Hz, does not follow the alternating sign rule since the shortest pathway corresponds to a 'W' arrangement of bonds and therefore, such coupling is expected to have a positive σ -transmitted component. It is noted that these two carbon atoms are also connected by the six-bond $C_{63}-C_{43}-C_{23}-C_{40}-C_{60}-C_{42}-C_{22}$ pathway, which is also formed by an even number of bonds. The main pathway for ${}^3J(C_{63},C_{42})$ corresponds to a *trans*-arrangement, which should also transmit a positive σ -component. Note that the FC term of ${}^2J(C_{63},C_{60})$ is $+1.19$ Hz, while the FC term of ${}^2J(C,C)$ in benzene as calculated in this work is -1.15 Hz, i.e., they are of opposite signs. It is known [49–51] that the FC term of two-bond couplings becomes more positive when there are important hyperconjugative interactions into the antibonding orbitals belonging to the coupling pathway, this result suggests that ${}^2J(C_{63},C_{60}) = +1.19$ Hz reflects the strain in the neighbor pentagon rings, which enhances hyperconjugative interactions like for instance, $(C_{42}-C_{22}) \rightarrow (C_{70}-C_{63})^*$. At this point it is important to recall [52] that the cage-like structure of a fullerene consists of 12 pentagon rings with hexagon rings in an amount that depends on the total number of carbon atoms. The 'isolated pentagon rule' [53,54], which holds true for most synthesized fullerene compounds, states that pentagon rings should be separated from each other to minimize strain.

In Table 4, a few long-range couplings whose pathways are transversal to the belt are shown. As expected, pathways crossing the symmetry plane are not efficient for transmitting the FC term of long-range couplings. For instance, ${}^9J(C_{10},C_1)$ is small and negative, suggesting that the $C_{10}-C_{20}-C_{32}-C_{52}-C_{62}-C_{42}-C_{22}-C_{36}-C_{11}-C_1$ pathway is very inefficient in transmitting the spin information associated with the π -component of the FC term. Obviously, similar considerations can be applied to ${}^8J(C_{20},C_1)$ and ${}^7J(C_{32},C_1)$ couplings. In all these three cases the coupling pathway includes two equivalent bonds that are adjacent, e.g., $C_{52}-C_{62}$ and $C_{62}-C_{42}$. Both bonds are equivalent for symmetry reasons. ${}^6J(C_{52},C_1)$ satisfies the alternating sign rule and is larger than the previous three. This shows that its main pathway is $C_{52}-C_{62}-C_{66}-C_{56}-C_{36}-C_{11}-C_1$, i.e., it does not involve two adjacent equal bonds. Similarly, one of the main pathways for ${}^5J(C_{62},C_1)$ is $C_{62}-C_{66}-C_{56}-C_{36}-C_{11}-C_1$. The four-bond pathway for ${}^4J(C_{42},C_1)$ is quite inefficient for transmitting

a σ -component and therefore, it is not surprising that it satisfies the alternating sign rule. The FC contribution to ${}^3J(\text{C}_{22}, \text{C}_1)$ is notably smaller than the similar coupling in benzene, where the FC term calculated in this work is 8.02 Hz (the experimental value of the ${}^3J(\text{C}, \text{C})$ in benzene was reported by Kaski *et al.* [41] as 10.111 Hz). The FC contribution to ${}^2J(\text{C}_{36}, \text{C}_1)$ is calculated as positive, which is indicative of the strain of neighbor pentagon rings (*vide supra*).

The main features of diamagnetic ring currents in C_{70} deduced from long-range $J(\text{C}, \text{C})$ couplings are nicely supported observing the different experimental ${}^{13}\text{C}$ chemical shifts reported by Johnson *et al.* [25], as discussed above. A similar analysis based on long-range $J(\text{C}, \text{C})$ couplings is carried out for C_{60} . A few examples are shown in Table 5, where several analogous couplings are compared for C_{60} and $\text{C}_{60}^{(6-)}$. The numbering of C atoms is displayed in Scheme 1. Since it is accepted that diamagnetic ring currents along a pentagon ring are inhibited, it is expected that coupling constants transmitted through pathways involving two adjacent pentagon bonds are inefficient for transmitting the π -component of long-range couplings. This suggests that one of the main ${}^{10}J(\text{C}_3, \text{C}_2)$ coupling pathways is $\text{C}_3\text{--C}_{17}\text{--C}_{41}\text{--C}_{23}\text{--C}_{47}\text{--C}_{45}\text{--C}_{21}\text{--C}_{37}\text{--C}_{13}\text{--C}_1\text{--C}_2$, being inhibited the coupling pathways involving an odd number of bonds like, for instance, $\text{C}_3\text{--C}_{17}\text{--C}_{54}\text{--C}_{30}\text{--C}_9\text{--C}_{29}\text{--C}_{53}\text{--C}_{13}\text{--C}_1\text{--C}_2$ and $\text{C}_3\text{--C}_4\text{--C}_{19}\text{--C}_{58}\text{--C}_{34}\text{--C}_{11}\text{--C}_{33}\text{--C}_{57}\text{--C}_{15}\text{--C}_2$. These last two pathways involve two adjacent pentagon bonds. Therefore, we expect their ability for transmitting the spin information associated with the π -component of the FC term in the $\text{C}_{60}^{(6-)}$ anion, to be enhanced. The result displayed in Table 5, ${}^{10}J(\text{C}_3, \text{C}_2) = +0.62$ Hz, is compatible with such a rationalization. Similar considerations hold for ${}^9J(\text{C}_3, \text{C}_1)$, where in $\text{C}_{60}^{(6-)}$ the eight-bond pathways are operating. Another interesting case is ${}^9J(\text{C}_{11}, \text{C}_9)$ in C_{60} where the eight-bond as well as the nine-bond pathways involve two-adjacent pentagon-bond sequence. Upon increasing in 6 the number of electrons, i.e., in

Table 5. Comparison between the FC contributions (in Hz) to several long-range couplings, ${}^nJ(\text{C}_i, \text{C}_j)$, in C_{60} and in $\text{C}_{60}^{(6-)}$

n	$J(\text{C}_i, \text{C}_j)$	C_{60}	$\text{C}_{60}^{(6-)}$
10	$J(\text{C}_3, \text{C}_2)$	-0.27	+0.62
9	$J(\text{C}_3, \text{C}_1)$	+0.35	-0.11
9	$J(\text{C}_{11}, \text{C}_9)$	-0.01	-0.10
8	$J(\text{C}_{33}, \text{C}_9)$	-0.00	+0.07
8	$J(\text{C}_{17}, \text{C}_1)$	-0.29	0.07
7	$J(\text{C}_{41}, \text{C}_1)$	+0.34	-0.12
7	$J(\text{C}_{46}, \text{C}_9)$	-0.00	+0.05
7	$J(\text{C}_{33}, \text{C}_{29})$	+0.34	+0.04
6	$J(\text{C}_{23}, \text{C}_1)$	-0.34	+0.18
6	$J(\text{C}_{22}, \text{C}_9)$	-0.00	-0.07
5	$J(\text{C}_{47}, \text{C}_1)$	+0.51	-0.12
4	$J(\text{C}_{46}, \text{C}_{23})$	-0.98	-0.43
3	$J(\text{C}_{21}, \text{C}_1)$	+3.63	+2.93
2	$J(\text{C}_{37}, \text{C}_1)$	+1.03	+2.51
1	$J(\text{C}_{13}, \text{C}_1)$	+58.8	+57.1

$C_{60}^{(6-)}$, both types of pathways are enhanced in their abilities for transmitting the π -component of the FC term. Since the calculated FC term is negative, ${}^9J(C_{11}, C_9) = -0.10$ Hz, and its absolute value is smaller than expected, it seems that there is a strong competition between pathways of different parity. Similar considerations hold for ${}^8J(C_{33}, C_9)$, ${}^7J(C_{46}, C_9)$, and ${}^6J(C_{22}, C_9)$ couplings. The behavior of ${}^8J(C_{17}, C_1)$, ${}^7J(C_{41}, C_1)$, ${}^7J(C_{33}, C_{29})$, ${}^6J(C_{23}, C_1)$, and ${}^5J(C_{47}, C_1)$ couplings is quite similar to those of ${}^{10}J(C_3, C_2)$ and ${}^9J(C_3, C_1)$. For instance in C_{60} , ${}^6J(C_{23}, C_1)$ is mainly transmitted by the six-bond $C_{23}-C_{47}-C_{45}-C_{21}-C_{37}-C_{13}-C_1$ coupling pathway and in $C_{60}^{(6-)}$ it is also transmitted through seven-bond coupling pathways like $C_{23}-C_{47}-C_{30}-C_9-C_{29}-C_{53}-C_{13}-C_1$. In the latter compound there seems to be a strong competition between the seven- and six-bond pathways, being more important the transmission through the pathways containing an odd number of bonds. The comparison between two different types of three-bond couplings in C_{60} and in $C_{60}^{(6-)}$ is also worthy of note. For instance, ${}^3J(C_{21}, C_1)$ corresponds to a *trans*-pathway, $C_{21}-C_{37}-C_{13}-C_1$. In the former compound, pathways involving an even number of bonds like $C_{23}-C_5-C_{22}-C_{39}-C_{15}-C_2-C_1$ are inhibited since they contain adjacent pentagon bonds. In the latter compound, the transmission through such pathway is enhanced, corresponding to a negative contribution. The resulting FC term of ${}^3J(C_{21}, C_1)$ is smaller in $C_{60}^{(6-)}$ than in C_{60} (+2.93 vs. +3.63 Hz). A similar effect is observed for a three-bond pathway involving the diagonal of a hexagon ring like the ${}^3J(C_{46}, C_6)$ coupling. In $C_{60}^{(6-)}$ six-bond pathways like $C_{46}-C_{22}-C_{39}-C_{37}-C_{21}-C_5-C_6$ are enhanced, reducing the total FC term from +3.94 to +2.48 Hz. ${}^2J(C_{21}, C_6)$ increases from +1.03 Hz in C_{60} to +2.51 Hz in $C_{60}^{(6-)}$. This effect is originated in both, an increase in the strain in a pentagon ring and an enhancement of a five-bond pathway like $C_{21}-C_{37}-C_{39}-C_{22}-C_5-C_6$, which should give a positive π -contribution to the FC term. The optimized pentagon bond length is somewhat shorter in the anion than in the neutral compound, 1.454 and 1.456 Å, respectively. It is important to point out that the π -transmitted contribution to the FC term of a two-bond coupling is negative.

4. CONCLUSIONS

Results presented in this work indicate that long-range ${}^nJ({}^{13}C, {}^{13}C)$ are remarkable probes to gauge diamagnetic ring currents in fullerenes. Without addressing explicitly the controversial topic about the aromaticity of fullerenes, the π -transmitted components of the FC contributions to such long-range couplings provide useful information about factors that either inhibit or enhance the circulation of diamagnetic ring currents. For instance, the equilateral ring pentagons inhibit diamagnetic ring currents both in C_{60} and in C_{70} . This behavior is observed as an inhibition of π -coupling pathways involving two adjacent bonds belonging to sides of equilateral pentagon rings. It is interesting to note that this inhibition is not present in the $C_{60}^{(6-)}$ anion. In C_{70} , diamagnetic ring currents are notably more preferential for pathways along the belt. Transversal diamagnetic ring currents are greatly hindered by the $C_1-C_2-C_3-C_4-C_5$ equilateral pentagon ring (and its symmetrical pentagon ring).

The FC term of ${}^2J({}^{13}\text{C}, {}^{13}\text{C})$ couplings provides interesting information about the distribution of strain tension in fullerenes. As reported previously, the main distinction to be made of *geminal* couplings is twofold. (a) Those whose coupling pathway involves two adjacent C–C bonds of pentagon rings. They are positive (~ 6 Hz) and correspond to two-pathway couplings, one of them being *geminal* and the second one *cis-vicinal*. They do not provide fundamental information concerning the molecular structure of fullerenes. (b) Those corresponding to a pathway involving two adjacent hexagon-ring bonds. Their absolute value is in general smaller than 2 Hz. They can provide interesting information about the local strain in this type of compounds, particularly, around a pentagon ring. A case in point is the following pair of FC contributions to *geminal* $J(\text{C}, \text{C})$ couplings in C_{70} : ${}^2\text{FC}(\text{C}_{56}, \text{C}_{46}) = 0.3$ Hz; and ${}^2\text{FC}(\text{C}_{36}, \text{C}_{66}) = 1.6$ Hz [32]. This suggests that, e.g., the $(\text{C}_{41}-\text{C}_{21}) \rightarrow (\text{C}_{56}-\text{C}_{66})^*$ hyperconjugative interaction is weaker than the $(\text{C}_{11}-\text{C}_1) \rightarrow (\text{C}_{36}-\text{C}_{56})^*$ interaction. This indicates that the strain around the $\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4-\text{C}_5$ equilateral pentagon ring is stronger than around the $\text{C}_{11}-\text{C}_{21}-\text{C}_{41}-\text{C}_{56}-\text{C}_{36}$ non-equilateral pentagon ring.

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