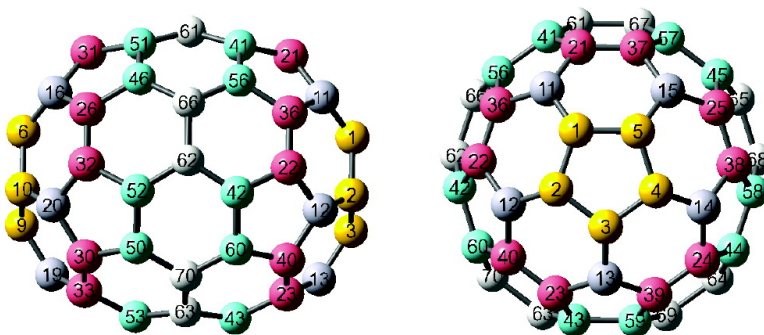Communication

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Density Functional Theory Calculation of Indirect Nuclear Magnetic Resonance Spin−Spin Coupling Constants in C_{70}

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The discovery of a new form of elementary carbon back in the 1980s[1] has attracted the attention of the scientific community ever since. Great effort has been made to elucidate the electronic structure and properties of fullerenes.[2] In this regard, nuclear magnetic resonance (NMR) is a unique tool for understanding the chemical structure of a given compound. For instance, the NMR spectrum of the C_{60} fullerene consists of a single line at 143 ppm demonstrating the equivalence of all C atoms, while the C_{70} NMR spectrum consists of 5 lines showing that only 5 out of the 70 carbon atoms are nonequivalent.[3] In 1991, Johnson et al.[4] reported a two-dimensional NMR study of the C_{70} fullerene in toluene-d_8. In that experiment, a single ^{13}C NMR line of a carbon is linked to that of its bonded neighbor, yielding the one-bond indirect carbon−carbon coupling constant, $^1J_{CC}$, between the five nonequivalent carbons in the C_{70} structure. These experimental results represent a unique opportunity to test state-of-the-art quantum chemistry calculations. From a computational point of view, spin−spin coupling constants are a difficult property to reproduce due to the nature of the perturbations involved.

Interactions of the nuclear magnetic moments and electrons in a nonrelativistic framework were first described by Ramsey.[5] There are four Hamiltonians describing such interactions, namely, the Fermi contact (FC), the spin dipolar (SD), the paramagnetic spin−orbital (PSO), and the diamagnetic spin−orbital (DSO). Generally, the FC contribution is the most important. However, to achieve quantitative agreement with experiment, all four contributions must be computed.[6−8] Density functional theory (DFT) represents a powerful tool for obtaining electronic structure and properties in medium- and large-sized compounds. In the past five years, many interesting works have appeared in which J coupling constants were evaluated within the DFT framework.[9] Although some problems arise when dealing with lone-pair-containing atoms, J_{CC} and J_{CH} values obtained with hybrid functionals are generally in good agreement with experimental values.[9,10] Recently, Jaszuński et al.[11] reported all the spin−spin couplings in C_{60} calculated within DFT. Unfortunately, due to the high symmetry of C_{60}, the corresponding J_{CC} values have not been measured, and therefore, comparison with experiment is not possible.

In this work, we present for the first time the calculation of all J_{CC} couplings in C_{70} by means of density functional theory and compare our results with the corresponding available experimental values. We have first optimized the C_{70} geometry in D_{5h} symmetry at the B3LYP/cc-pVDZ level. This basis set, although reasonably good for geometry optimizations, is not suitable for J coupling calculations. It was shown that the calculation of these parameters critically depends on the quality of the basis set employed.[7,12,13] Therefore, we have tested different basis sets for the J coupling calculations: the EPR-II[14] basis set, the EPR-II-sd basis (consisting

Scheme 1. Longitudinal and Axial Views of the C_{70} Fullerene[a]
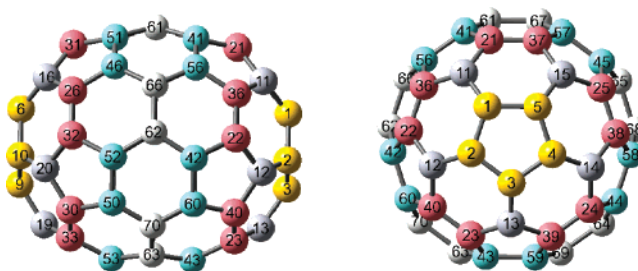
[a] The five different colors represent the five nonequivalent C atoms.

Table 1. $^1J_{CC}$ (Hz) between the Five Nonequivalent Carbon Atoms in C_{70} (C_1, C_{11}, C_{36}, C_{56}, C_{66})

method/basis set	$^1J_{1-11}$	$^1J_{11-36}$	$^1J_{36-56}$	$^1J_{56-66}$	functions[b]
BLYP/EPR-II	71.0	57.0	56.7	63.4	1190
BLYP/EPR-II-sd	62.1	49.8	49.6	55.5	1470
BLYP/cc-pCVDZ-sd	63.1	50.6	50.4	56.4	1680
B3LYP/EPR-II	76.5	61.6	61.2	68.3	1190
B3LYP/EPR-II-sd	67.1	54.0	53.6	59.9	1470
B3LYP/cc-pCVDZ-sd	68.4	55.0	54.7	61.1	1680
experimental value[a]	**68**	**55**	**55**	**62**	

[a] From ref 4. [b] Total number of basis functions employed in the calculation.

in the EPR-II basis set with all s functions decontracted), and the cc-pCVDZ[15] basis set with all the s functions decontracted, namely, cc-pCVDZ-sd. These bases are characterized by having an enhanced s part to better describe the nuclear region, which is particularly important to compute the FC contribution.

Among all available density functionals, the hybrid B3LYP[16] (that contains a portion of Hartree−Fock exchange) has been shown to provide good results for spin−spin couplings.[7−9,12] However, the computation of Hartree−Fock exchange makes hybrid functional calculations more time-consuming than calculations using generalized gradient approximation functionals (GGA). In this communication, we compare results from the BLYP[17] (GGA) and the hybrid B3LYP functionals obtained with the *Gaussian 03* program.[18]

There are 143 distinct coupling constants, $^nJ_{CC}$, in the C_{70} fullerene (due to the high symmetry, there are only 23 distinct couplings in C_{60}). To limit space, in this communication we only present one-bond ($^1J_{CC}$) and two-bond ($^2J_{CC}$) couplings. Calculated values of longer range $^nJ_{CC}$ ($n > 2$) can be found in Supporting Information.

In Scheme 1, we observe the longitudinal and axial views of the C_{70} fullerene. The five nonequivalent C atoms (C_1, C_{11}, C_{36}, C_{56}, and C_{66} in Scheme 1) are shown in different colors to emphasize the layered structure of C_{70}.

In Table 1, we present the one-bond coupling constants between the five nonequivalent C atoms in C_{70} calculated using different levels of theory. We observe that even when the hybrid B3LYP

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Table 2. FC, SD, PSO, and DSO Contributions to One-Bond and Two-Bond Carbon−Carbon Indirect Spin−Spin Coupling Constants (Hz) in C_{70} Calculated at the B3LYP/cc-pCVDZ-sd Level

J_{CC}	FC	SD	PSO	DSO	total	experimental value
$^1J_{1,2}$	58.5	0.7	−4.7	0.4	**54.9**	
$^1J_{1,11}$	73.6	1.5	−7.1	0.4	**68.4**	**68**
$^1J_{11,36}$	58.6	0.7	−4.7	0.4	**55.0**	**55**
$^1J_{36,22}$	70.9	1.5	−7.2	0.4	**65.7**	
$^1J_{36,56}$	58.1	0.7	−4.5	0.4	**54.7**	**55**
$^1J_{56,41}$	64.0	1.1	−5.9	0.4	**59.7**	
$^1J_{56,66}$	65.7	1.0	−6.0	0.4	**61.1**	**62**
$^1J_{66,62}$	59.7	0.6	−4.5	0.4	**56.3**	
$^2J_{1,4}$	6.4	−0.1	−0.2	0.2	**6.3**	
$^2J_{1,12}$	1.3	−0.2	−0.2	0.1	**1.0**	
$^2J_{1,21}$	1.3	−0.3	−0.2	0.1	**1.0**	
$^2J_{11,22}$	1.1	−0.3	−0.2	0.1	**0.8**	
$^2J_{11,56}$	6.5	0.0	−0.3	0.2	**6.4**	
$^2J_{36,21}$	6.8	0.0	−0.2	0.2	**6.8**	
$^2J_{36,41}$	6.2	−0.1	−0.2	0.2	**6.0**	
$^2J_{36,66}$	1.6	−0.3	−0.2	0.1	**1.2**	
$^2J_{56,22}$	1.4	−0.3	−0.1	0.1	**1.1**	
$^2J_{56,46}$	0.3	−0.7	−0.2	0.2	**−0.4**	
$^2J_{56,61}$	1.1	−0.3	−0.2	0.1	**0.8**	
$^2J_{56,62}$	1.2	−0.2	−0.2	0.2	**0.9**	

[a] Experimental values from ref 4.

functional performs better than the BLYP functional, the choice of basis set is critical. Both cc-pCVDZ-sd and EPR-II-sd basis sets produce J couplings in excellent agreement with experimental values. Particularly, the cc-pCVDZ-sd basis set has been shown to produce J_{CC} couplings close to the basis set limit in ethane.[12] Vibrational corrections to J couplings in this compound are assumed to be small. In a recent study, Ruden et al. demonstrated that vibrational corrections for J_{CC} in benzene are smaller than 1 Hz.[19]

In Table 2, all $^1J_{CC}$ and $^2J_{CC}$ values calculated at the B3LYP/cc-pCVDZ-sd level are displayed. $^1J_{CC}$ couplings involving pairs of border belt atoms seem to form two alternating carbon chains (which are equal to each other due to symmetry reasons). The unit of the carbon chain can be appreciated in Scheme 1. This unit is constructed from the sequence $C_{41}-C_{56}-C_{36}-C_{22}$ (the specular image is $C_{51}-C_{46}-C_{26}-C_{32}$). One-bond couplings along this unit are 59.7, 54.7, and 65.7 Hz, respectively. Their FC, SD, and PSO contributions are typical of a conjugating C−C bond sequence.[9] The corresponding bond lengths (at the B3LYP/cc-pVDZ level) are 1.437, 1.451, and 1.391 Å, in agreement with experimental values and previous calculations at the Hartree−Fock level.[20,21] This suggests the presence of two opposite ring currents along the belt borders. Within this electronic structure picture, carbon atoms inside the ring are expected to show an important shielding effect, while those outside should exhibit a deshielding effect. The corresponding experimental chemical shifts[4] are 130.8 ppm for C_{66} (inside the ring) and 150.8 pmm for C_{11} (outside the ring), in agreement with this picture.

Calculated $^2J_{CC}$ in C_{70} can be separated in two groups according to their values, i.e., those ranging from 6.0 to 6.8 Hz and those ranging from −0.4 to 1.2 Hz. The larger values of couplings for the first group can be easily rationalized since they correspond to $^2J_{CC}$, whose coupling pathways involve two bonds of a pentagon. Such couplings are connected by a two-bond and a three-bond pathway. All except one $^2J_{CC}$ belonging to the second group are small but positive suggesting important hyperconjugative interactions taking place in C_{70}.[10] To the best of the authors' knowledge, $^2J_{CC}$ in C_{70} have not been reported in the literature.

In summary, we have calculated all indirect spin−spin coupling constants in the C_{70} fullerene. Our calculations of $^1J_{CC}$ between the five nonequivalent carbon atoms are in excellent agreement with the corresponding experimental values. These benchmark calculations indicate that theoretical predictions of spin−spin coupling constants would provide a powerful tool for structural identification, particularly in fullerene compounds.

Supporting Information Available: All $^nJ_{CC}$ coupling constants calculated at the B3LYP/cc-pCVDZ-sd level in C_{70}. This material is available free of charge via the Internet at http://pubs.acs.org.

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