Density Functional Theory Study of ^{14}N Isotropic Hyperfine Coupling Constants of Organic Radicals

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Nitrogen hyperfine coupling constants (hfccs) of organic radicals have been calculated by density functional theory (DFT) methodology. The capability of the B3LYP functional, combined with 6-31G*, TZVP and EPR-III basis sets, to reproduce experimental nitrogen coupling constant data has been analyzed for 109 neutral, cationic and anionic radicals, all of them containing at least one nitrogen atom. The results indicate that the selection of the basis set plays an important role in the accuracy of DFT calculations of hfccs, mainly in relation with the composition of the primitive functions and the quantum number of those functions. The main conclusion obtained is the high reliability of the scheme B3LYP/6-31G* for the prediction of nitrogen hfccs with very low computational cost.

Introduction

Radicals containing nitrogen atoms play an important task in many processes of physical, chemical and biological interest.[1] The nuclear hyperfine interaction provides information about the electronic distribution in those systems and is experimentally measured by electron paramagnetic resonance (EPR) technique. The isotropic term (a_{iso}), so-called isotropic hyperfine coupling constant (hfcc), is a function of the Fermi contact interaction of the unpaired electron with a determined nucleus, and strongly depends on the spin density at the nucleus position. From the theoretical point of view, it is well-known that unrestricted Hartree−Fock (UHF) isotropic coupling constants are grossly overestimated, whereas the computed values of the anisotropic term seem to be quite reasonable. The isotropic term, which is much more difficult to compute in quantitative agreement with the experimental data than the corresponding anisotropic term, has received great attention from theoretical chemists and physicists. This is due to the fact that this property is very sensitive to the quality of the wavefunction and to the level of the calculation, because the hfcc depends on the electron correlation, the one-electron basis set, and the use of a very adequate molecular geometry.

In previous papers,[2] we investigated the reliability of density functional theory (DFT) methodology to calculate the isotropic hfccs of different nuclei on the ground state of a large number of both organic and inorganic radicals. Different functionals and basis sets were considered for determining the best computational scheme. As expected, theoretical values of the a_{iso} resulted to be dependent on the calculation level and the basis set size. The main conclusion was that the best overall results are obtained when the B3LYP functional is combined with the TZVP or EPR-III basis set, yielding highly accurate values of hfccs. However, a detailed analysis of all these data showed that the nitrogen a_{iso} did not follow this general behavior. For the 16 nitrogen hfccs calculated,[2a] the best fit was reached when the 6-31G* and EPR-III basis sets were used, whereas the worst fit was obtained for cc-pVQZ, and intermediate values were found for the TZVP basis set. A partial regression analysis for this nucleus is not significant due to the small number of computed hfccs. A behavior similar to that of the nitrogen a_{iso} was also observed for ^{17}O hfccs, but in this case, a representative sample set is not available, due to the lack of experimental data.

For this reason, the aim of this paper is to fill this lack by investigating the performance of DFT methodology to predict, with a certain degree of accuracy, the isotropic hfccs of radicals containing a ^{14}N nucleus. To establish a better methodology to predict the nitrogen a_{iso}, we have carried out in this work an extensive study using the B3LYP method and different basis sets for the calculation of 116 nitrogen hfccs of radicals belonging to a wide range of chemical families. The main goal has been achieved using a statistical analysis by comparing the calculated a_{iso} (^{14}N) with the experimental ones. This paper should be a useful tool for EPR spectroscopists, because it should facilitate the correct assignment of the experimental hfccs from theoretical values.

Nitrogen Atom

The second-row elements B−F have unpaired electrons that are analogous to molecular π-radicals. This feature implies potential complications to the study of these systems, being a particular challenge for theoretical chemists. Before studying the nitrogen-containing radicals, we considered it of interest to carry out a study of the nitrogen atom, analyzing the values of a_{iso} for the ground state (^4S) of ^{14}N with different theoretical approaches. Many theoretical studies of the nitrogen atom hfccs have been carried out by several authors,[3−12] who have concluded that the obtained value is influenced by the flexibility of the basis set at different levels of calculation.

The early theoretical works on the second-row atom spin densities and related properties were published by Desclaux[3] and Hibbert.[4] In this latter paper, Glass and Hibbert[4b] computed a_{iso} for the second-row atoms using configuration interaction (CI) wavefunctions, studying the influence of the number of excitations.

Engels et al.[5] underscored the importance of a multireference configuration interaction (MRCI) treatment of electron correla-

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tion. They analyzed the effects of the basis set and the CI methodology. Their works provide a detailed analysis of the charge density at the nucleus and the spin polarization in the 1s and 2s shells as a function of the CI parameters. They found the dependence of hfcc on the basis set size, concluding that small basis sets are not appropriate for an a_{iso} calculation because their virtual space is not able to provide a good description of the polarization of the 1s and 2s shells. They also concluded that larger basis sets have more flexibility and are therefore able to give a more balanced description of the 1s and 2s spin polarization. Functions of a higher quantum number than s make no direct contribution to a_{iso} but describe correlation effects. The importance of polarization functions was clearly demonstrated by Knight et al.[6] They obtained contributions from d and f functions based on selected MRCI calculations with large basis sets and concluded that hfcc increased monotonically as angular momentum was saturated. Feller and Davidson[7] achieved an excellent agreement with the experimental value for nitrogen atom (^{4}S) by using uncontracted even-tempered basis sets.

Bauslicher et al.[8] studied a_{iso} of the nitrogen atom using complete active space self-consistent-field multireference configuration interaction (CASSCF/MRCI), multireference singles and doubles configuration interaction (MRSDCI), average coupled pair functional (ACPF), and full configuration interaction (FCI) wave functions, exploring a variety of basis sets. They concluded that the a_{iso} (^{14}N) is very sensitive to the kind of basis sets used and especially to the use of diffuse functions. This atom presents, as the rest of the atoms of this row, large 1s and 2s contributions and with opposite sign. For this reason, the valence orbitals and the correlation can provide a balanced treatment for the final value. Because the spin-densities depend critically on core correlation, it is thus surprising that the FCI calculations also indicate that high levels of correlation treatment are required for quantitative results of a_{iso}. The addition of a single diffuse s function increases hfcc dramatically, but the result is not sensitive to the specific value of the diffuse exponent. The diffuse function is very important because configurations involving 2s to 3s excitations with a recoupling in the 2p shell are extremely important for determining the 2s contribution to the spin density. This contribution to a_{iso} is underestimated unless diffuse functions are present to properly describe the relatively diffuse 3s orbital. Therefore, the importance of the diffuse functions seems to have been overlooked in the above-mentioned. They concluded that all the correlation energy must be taken into account and that at least a TZP basis and moderately large CI reference spaces are required to balance core and valence effects.

Chipman[9] calculated systematically Fermi contact spin densities of the second-row atoms B−F. He found that spin polarization of the 1s, 2s and 2p shells together with orbital polarization of the 2s shell are the important effects. Both core and valence contributions are large in magnitude but nearly cancel one another, leading to much smaller net spin densities. Carmichael[10] studied the performance of many body perturbation theory (MBPT) and coupled-cluster doubles (CCD) methods, in second-row element spin density calculations using extended basis sets. Using a higher level calculation, CCSD(T), the closest agreement with experiment was obtained, except for the nitrogen atom. Perera et al.[11] obtained accurate values of a_{iso} for the second-row atoms using ab initio techniques of the highest levels.

On the other hand, DFT methodology computing hfccs for this series of atoms has been applied by Barone[12] using an extended basis set and several functionals, and using the B3LYP functional with different basis sets. He concluded that a_{iso} are very sensitive to the functional form, and that the B3LYP functional needs large basis sets to obtain accurate values.

TABLE 1: B3LYP Isotropic Hyperfine Coupling Constants (*G*) for the Ground State ^{4}S of the Nitrogen Atom, Calculated with the 6-31G*, TZVP, EPR-III and cc-pVQZ Basis Sets, and 5 or 6 Components of d Functions

	a_{iso} (theoretical)				experimental	
	6-31G*	TZVP	EPR-III	cc-pVQZ	a_{iso}	ref
5d functions	8.88	1.34	3.49	−1.48	3.73	18
6d functions	2.60	1.70	3.68	2.20		

The above summary illustrates the complexity of computing a_{iso} for the nitrogen atom. A careful choice of the basis set, including diffuse and polarization functions, and an extensive treatment of the correlation problem is required. For this reason, we have considered of interest to compute the a_{iso} for its ground state (^{4}S) before performing the molecular study. This study was carried out by means of the B3LYP functional[13] and the four basis sets used in our previous work,[2a] namely, 6-31G*,[14] TZVP,[15] EPR-III[16] and cc-pVQZ.[17] The theoretical hfccs for the nitrogen atom, in Gauss, are summarized in Table 1, where the values obtained with five or six components for d functions in each basis set are shown. In general, the use of five functions furnishes a good value for EPR-III but it is a bad approach for the rest of the basis sets tried: 6-31G* overestimates the a_{iso} value, TZVP yields a theoretical value half of the experimental one and cc-pVQZ gives negative a_{iso} with a small absolute value. However, when six functions are employed, the theoretical a_{iso}^{N} is improved for the four basis sets obtainig closer values to the experimental one, 3.73 G.[18] The theoretical value computed with the EPR-III basis set shows very good agreement with the experimental one for both cases (five or six d functions), whereas the results with the TZVP basis set remains poor. The most surprising data are obtained for the other two basis sets: using six d functions, cc-pVQZ modifies deeply the theoretical value of a_{iso}, becoming positive and reasonably close to the experimental one, and the 6-31G* basis set improves considerably the result when six d functions are employed (2.60 G). We have often observed that simply increasing the basis set size does not automatically improve the agreement with experimental data. We have discarded the large basis set cc-pVQZ for the study of ^{14}N nucleus hfccs of the radicals considered in this paper, on the basis of these atomic results, the partial regression analysis of the a_{iso} (^{14}N) on ref 2a (see above), and taking into account that the standard programs for the calculation of molecular structures use five d functions for TZVP, EPR-III and cc-pVQZ, and six d functions for 6-31G* basis set.

Computational Details

We have considered a set of 109 paramagnetic species containing at least one ^{14}N ($I = 1$) nucleus with known experimental hfcc. The studied set comprises neutral, cationic and anionic nitrogen radicals. In the present work, hfccs of the radicals are calculated using the B3LYP hybrid functional with the three aforementioned basis sets: 6-31G*, TZVP, and EPR-III. The first one is a small double-ζ basis plus polarization, whereas the second one is a DFT-optimized valence triple-ζ basis. The latter is an optimized basis set for the computation of hfccs by DFT methods, and larger: triple-ζ basis including diffuse functions, double d-polarizations and a single set of f-polarization functions.

The structures of the 109 radicals are depicted in Figure 1. Schemes of compounds **58**, **59** and **63** correspond to both anion

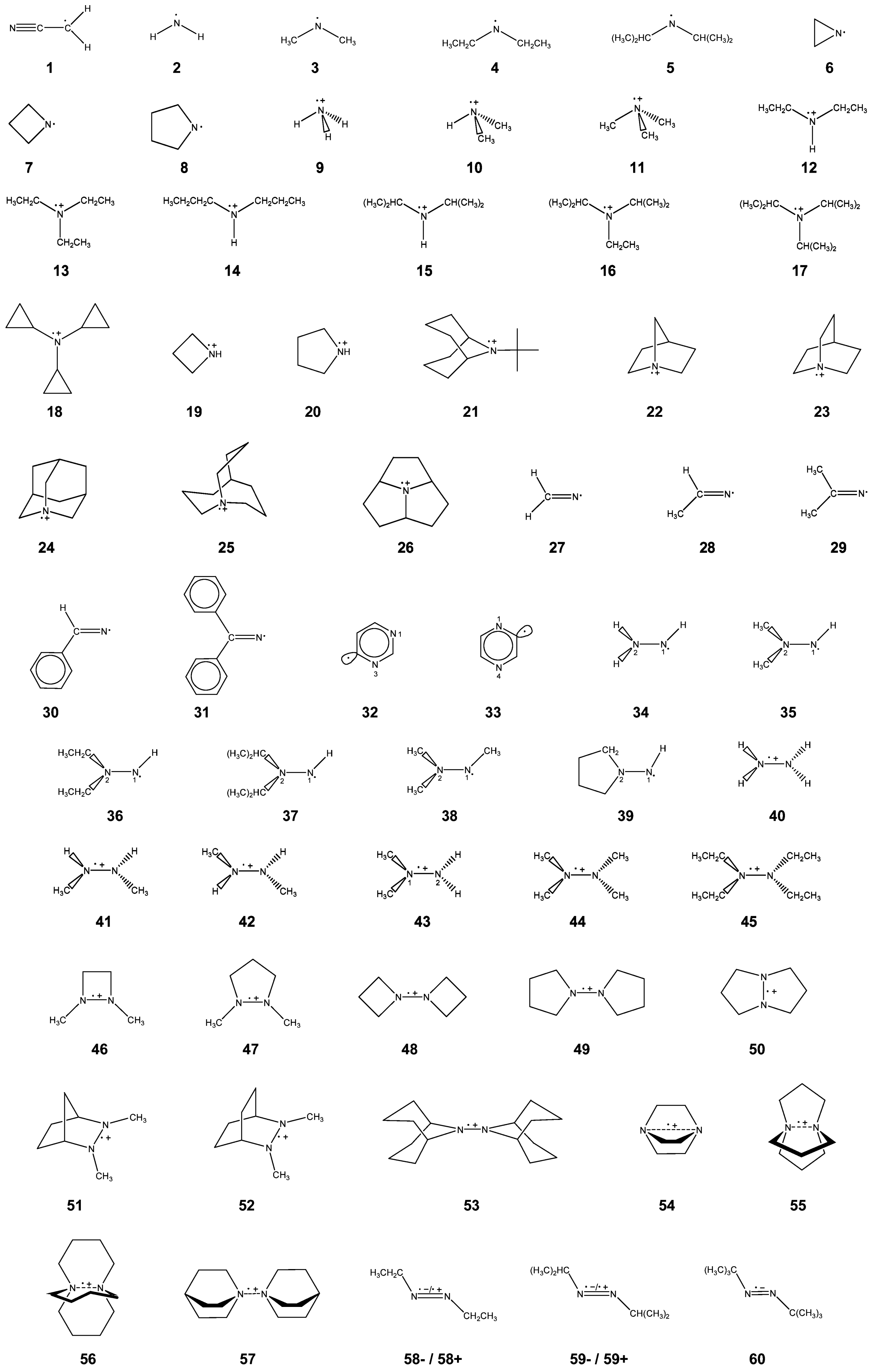

Figure 1. Part 1 of 2.

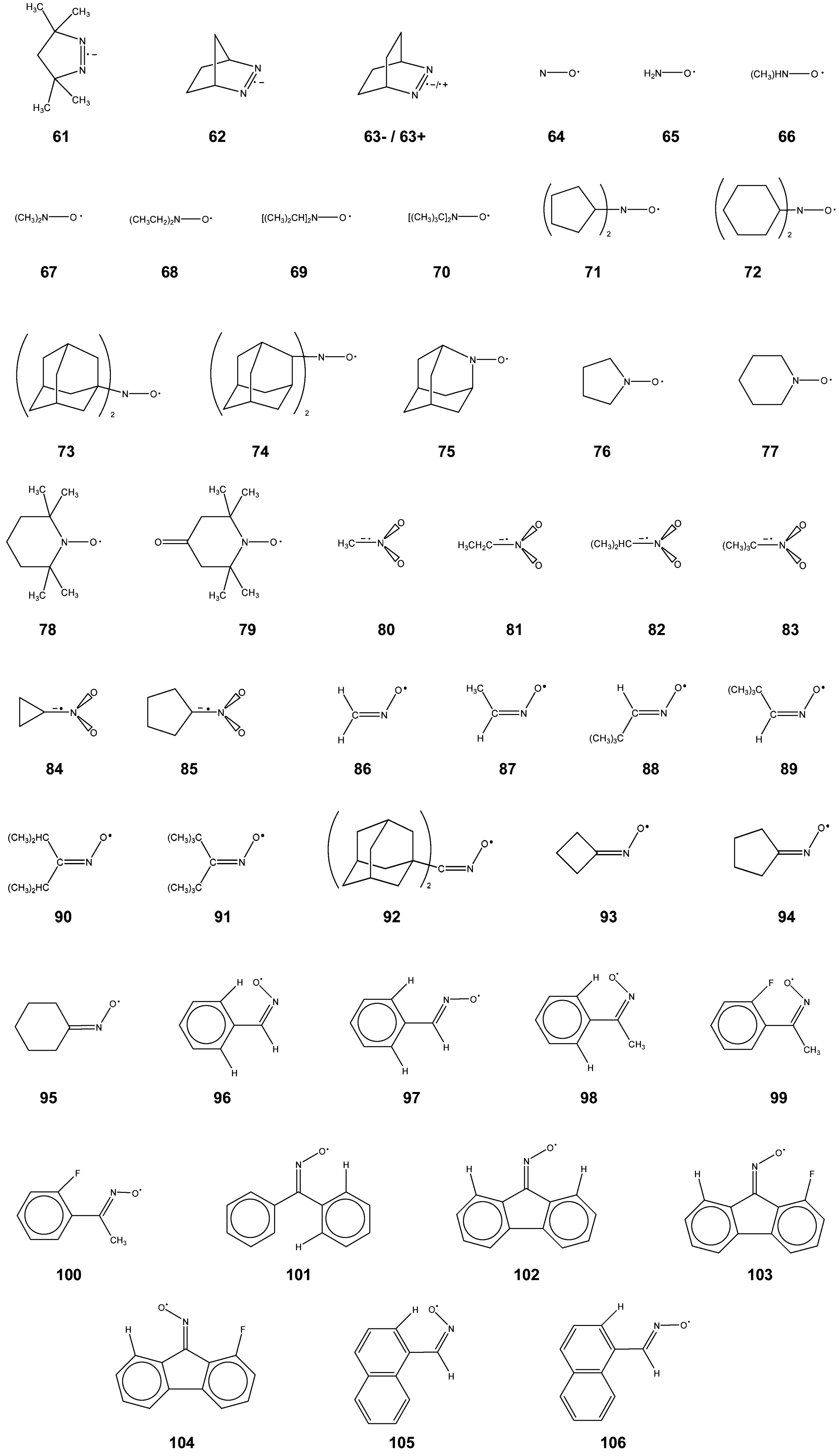

Figure 1. Structures of the radicals studied.

and cation radicals, indicated with a minus or plus symbol, respectively. Due to the large number of nitrogen-containing radicals studied, we have ordered them by functional organic group criteria. All of them are organic radicals centered on one, two or three atoms. The cyanomethyl radical (**1**) is a C-centered radical. Radicals **2**−**33** correspond to N-centered radicals: alkylaminyl radicals (**2**−**8**); radical cations of acyclic alkylamines (**9**−**18**); radical cations of cyclic alkylamines (**19**−**26**); iminyl radicals (**27**−**31**); azaphenyl radicals (**32** and **33**). Radicals **34**−**63** correspond to NN-centered radicals: alkylhydrazyl radicals (**34**−**39**); radical cations of alkylhydrazines (**40**−**53**); radical cations of alkyldiamines (**54**−**57**); radical ions of alkylazoalkanes (**58**−**63**). Radicals **64**−**106** correspond to NO- and NO_2-centered radicals: alkylnitroxyl radicals (**64**−**79**); radical anions of nitroalkanes (**80**−**85**); alkaniminoxyl radicals (**86**−**95**); araniminoxyl radicals (**96**−**106**).

Molecular geometries are fully optimized at the B3LYP level employing the 6-31G* basis set to maintain the same criteria used in ref 2 due to its low computational cost. We have analyzed the vibrational frequencies for warranting that the optimized structures correspond to a minimum of energy.

The name, the symmetry of the electronic ground state, and the total energies corresponding to the minimum of each radical at the following levels: B3LYP/6-31G*//B3LYP/6-31G*, B3LYP/TZVP//B3LYP/6-31G* and B3LYP/EPR-III//B3LYP/6-31G*, are shown in Table S1 (see Supporting Information).

Although geometry plays an important role in the calculation of hfccs, the selected radicals present, in general, well-defined geometries for their ground states. The effects of vibrational average on the calculated a_{iso} have not been considered in this study because the majority of these radicals are very large. A total of 116 hfccs of ^{14}N nuclei have been analyzed. All computations are performed using the spin-unrestricted theory of the Gaussian program.[19]

Results and Discussion

The calculated and experimental a_{iso} (in Gauss) of nitrogen nuclei are summarized in Table 2. This table has seven columns. The first one corresponds to the number of each radical. In the second column the nitrogen nuclei appear marked with a previous number (2) to indicate the equivalent atoms, and with a subindex to identify the nonequivalent atoms unequivocally, when necessary. The following three columns report the theoretical hfcc values obtained with the schemes (A) B3LYP/6-31G*//B3LYP/6-31G*, (B) B3LYP/TZVP//B3LYP/6-31G* and (C) B3LYP/EPR-III//B3LYP/6-31G*. In the last two columns, the experimental hfccs are given and their references are summarized. As is well-known, the sign of a_{iso} is not determined by an EPR experiment. The corresponding sign is assigned on the basis of theoretical results. All experimental a_{iso} of this table have been assigned with positive sign excepting the five data explicitly indicated.

The general behavior obtained in the present calculations is commented below. The main characteristic of values for nitrogen a_{iso} is that the sign of all theoretical data is positive with a range of values between ca. 8 and 33 G, with a unique exception for the radical **1**.

N-Centered Radicals. Aminyl and iminyl radicals show excellent correlation using the 6-31G* basis set and a poor correlation for TZVP basis set. For the rest of the radicals of this series, radical cations of acyclic and cyclic alkylamines the theoretical hfccs are lower than experimental one, being the 6-31G* hfccs closer to the experimental ones than the other theoretical values. The TZVP basis set yields the poorest values. According to our results, the sign assigned to the experimental values of nitrogen hfccs[22,25,26] of radicals **3** and **9** is wrong. For the largest radical of each group of this series (**18**, **26** and **33**), theoretical and experimental values present a notable discrepancy. As explained above, the cyanomethyl radical is the only C-centered radical considered. For this reason this nitrogen nucleus presents a small value of a_{iso}, which is in good agreement with the experimental hfcc and the calculated value with the EPR-III basis set. Nitrogen a_{iso} of the alkylamine cation radicals (**9** to **26**) are higher than the rest of this series (see Table 2).

NN-Centered Radicals. Alkylhydrazyl radicals give a good correlation between experimental and theoretical hfccs, in particular when the 6-31G* basis set is employed. In the case of the hydrazyl radical (**34**), the theoretical value obtained indicates that the previous assignment of both nitrogen nuclei hfccs is interchanged.[41] As in the above cations, we have obtained theoretical values smaller than the experimental ones for the alkylhydrazine radical cations (**40**−**53**). The best fit is obtained when the 6-31G* basis set is used. As indicated for hydrazyl radical, the previous assignment of the nitrogen hfccs for radical **43** is wrong, on the basis of our calculations.[47] For alkyldiamine cations, the three theoretical values are very similar and are not in good agreement with previous experimental data except for the smallest radical of this series (**54**). For the alkylazoalkane radical ions, the agreement between experimental and theoretical results is excellent when the 6-31G* basis sets is employed, with the exception of **58** and **59** radical cations.[56] As in the above series, higher values for nitrogen a_{iso} are computed and measured for cation radicals.

NO- and NO_2-Centered Radicals. In general, we have obtained a good agreement with the experimental data using the 6-31G* basis set. For animinoxyl radicals (**86**−**106**), the three basis sets yield very similar values. We also remark that for some alkylnitroxyl radicals (**68**, **69**, **72** and **76**) larger discrepancies between experimental and theoretical values using the TZVP and EPR-III basis sets, are obtained. The nitrogen oxide (**64**) presents a significant discrepancy and it has been previously analyzed by Eriksson et al.[86] They concluded that the NO radical does not exhibit any EPR signal due to the fact that its ground state is Π state with two possible values of angular momentum j (1/2 and 3/2), whereas an average state of the density is computed with DFT. We stress that the radicals centered on three atoms (anions of nitroalkanes) present very good agreement between experimental and theoretical hfccs when the 6-31G* basis set is used.

The NO- and NO_2-radicals present both theoretical and experimental nitrogen a_{iso} values larger than those corresponding to the previous series. Animinoxyl radicals are localized in the nitrogen atom, because their values are higher than 30 G for the nitrogen atom. It is interesting to remark that for radicals with available experimental ^{17}O a_{iso} (**70**, **78**, **79** and **91**), the hfccs of ^{14}N and ^{17}O nuclei have similar values for each radical, although with the reverse sign (−19.41, −18.05, −19.29 and −22.6 G, respectively). Taking into account that a_{iso} is proportional to the electron density, with proportional factors of +115.3 and −216.3 for nitrogen and oxygen,[2a] respectively, we can conclude that the localization of the unpaired electron in the NO bond is on the nitrogen atom.

Regression Analysis. A regression analysis has been carried out for the three computational levels included in Table 2. In Figures 2−4, we depict the calculated a_{iso}(G) with the B3LYP functional and the 6-31G*, TZVP and EPR-III basis sets, respectively, versus the experimental a_{iso} (G) of the nitrogen

TABLE 2: Theoretical Hyperfine Coupling Constants (*G*) of ^{14}N Nuclei of the Radicals Studied at the Following Levels: [A] B3LYP/6-31G*//B3LYP/6-31G*; [B] B3LYP/TZVP//B3LYP/6-31G*; [C] B3LYP/EPR-III//B3LYP/6-31G*

		a_{iso} (theoretical)			experimental	
no.	nuclei	[A]	[B]	[C]	a_{iso}	ref
1	^{14}N	4.8	2.7	3.6	3.51	20
2	^{14}N	11.9	7.8	10.1	9.95	21
3	^{14}N	15.2	10.6	12.5	-14.78^{a}	22
4	^{14}N	14.8	10.4	12.1	14.27	22
5	^{14}N	15.0	10.7	12.5	14.31	22
6	^{14}N	13.0	8.5	10.7	12.52	23
7	^{14}N	14.8	9.9	11.8	13.99	23
8	^{14}N	15.4	10.6	12.4	14.3	24
9	^{14}N	18.7	13.3	15.0	-19.6^{a}	25, 26
10	^{14}N	17.3	12.8	14.3	19.28	27
11	^{14}N	18.4	14.0	15.6	20.7	28
12	^{14}N	17.1	12.6	14.1	18.65	27
13	^{14}N	18.4	14.2	15.7	20.8	29
14	^{14}N	15.6	11.7	13.0	18.58	27
15	^{14}N	16.6	12.6	13.9	18.7	27
16	^{14}N	18.4	14.4	15.7	20.2	30
17	^{14}N	18.7	14.7	16.1	20.2	30
18	^{14}N	13.2	10.3	11.4	20.1	31
19	^{14}N	17.5	13.0	14.4	19.1	32
20	^{14}N	17.0	12.5	14.0	20	24
21	^{14}N	17.5	13.8	15.1	19.5	33
22	^{14}N	26.8	25.8	26.7	30.2	34
23	^{14}N	22.0	20.5	21.4	25.1	34
24	^{14}N	19.3	17.4	18.3	21.6	34
25	^{14}N	17.2	13.5	14.8	19.2	30
26	^{14}N	20.9	18.3	19.5	25.0	35
27	^{14}N	10.0	6.2	8.3	9.8	36
28	^{14}N	10.3	6.3	8.3	10.20	37
29	^{14}N	10.8	6.5	8.4	9.6	36
30	^{14}N	10.8	6.6	8.5	11.3	38
31	^{14}N	11.0	6.7	8.6	10	39
32	^{14}N$_3$	29.1	33.7	32.4	28	40
33	^{14}N$_1$	30.5	35.0	33.6	28	40
34	^{14}N$_1$	12.0	8.5	10.3	8.8^{b}	41
	^{14}N$_2$	12.6	10.9	11.1	11.7^{b}	
35	^{14}N$_1$	11.1	7.3	8.7	9.60	42
	^{14}N$_2$	12.4	11.0	11.7	11.49	
36	^{14}N$_1$	11.3	7.5	8.7	9.58	42
	^{14}N$_2$	11.6	10.0	10.6	11.14	
37	^{14}N$_1$	9.8	7.5	8.7	9.95	42
	^{14}N$_2$	11.3	7.9	8.7	11.66	
38	^{14}N$_1$	12.5	8.9	10.3	11.7	43
	^{14}N$_2$	11.2	9.4	9.9	10.5	
39	^{14}N$_1$	10.9	7.2	8.5	10.6	44
	^{14}N$_2$	7.9	6.1	7.0	10.6	
40	2^{14}N	12.0	8.8	9.8	11.60	45
41	2^{14}N	12.2	9.2	10.1	14.7	46
42	2^{14}N	12.5	9.6	10.5	13.03	46
43	^{14}N$_1$	15.7	12.7	13.9	16.05^{b}	47
	^{14}N$_2$	10.8	8.1	8.7	9.69^{b}	
44	2^{14}N	12.4	9.5	10.4	13.38	47
45	2^{14}N	11.1	8.4	9.3	13.15	48
46	2^{14}N	13.2	10.5	11.3	15.0	49
47	2^{14}N	12.5	9.7	10.6	15.0	48
48	2^{14}N	13.2	10.7	11.5	14.8	48
49	2^{14}N	11.4	8.6	9.5	12.9	48, 49
50	2^{14}N	16.5	14.8	15.5	17.6	48, 49
51	2^{14}N	15.0	13.3	14.0	16.0	48
52	2^{14}N	12.0	9.3	10.1	13.9	48
53	2^{14}N	12.4	10.0	10.8	13.3	50
54	2^{14}N	16.6	17.0	17.1	16.96	51
55	2^{14}N	11.7	10.1	10.9	14.7	52
56	2^{14}N	29.8	30.8	30.8	35.9	53
57	2^{14}N	29.9	31.9	31.8	38.7	54
58−	2^{14}N	8.1	5.8	6.6	7.75	55
58+	2^{14}N	13.9	11.3	12.1	21	56
59−	2^{14}N	8.6	6.2	6.7	8.0	55
59+	2^{14}N	12.6	10.2	10.9	20	56
60	2^{14}N	8.9	6.4	7.2	8.24	57
61	2^{14}N	9.5	7.1	7.4	9.23	58
62	2^{14}N	9.1	6.5	6.9	8.55	58
63−	2^{14}N	9.3	6.8	7.5	8.76	58
63+	2^{14}N	31.0	34.0	33.1	31.4	59, 60
64	^{14}N	6.5	4.7	6.6	10.6	61
65	^{14}N	12.8	10.4	11.1	-11.9^{a}	62
66	^{14}N	13.3	11.1	11.9	13.8	62
67	^{14}N	15.0	13.0	14.0	15.2	62
68	^{14}N	14.8	12.6	13.6	16.7	63
69	^{14}N	12.3	10.0	11.1	15.9	63
70	^{14}N	13.9	11.8	12.7	16.2	64
71	^{14}N	13.3	10.9	11.9	14.9	65
72	^{14}N	10.7	8.3	9.4	14.4	66
73	^{14}N	13.6	11.4	12.3	15.2	67
74	^{14}N	14.1	11.5	12.5	14.1	68
75	^{14}N	17.6	16.7	17.1	-19.75^{a}	69
76	^{14}N	10.1	7.7	8.9	16.6	70
77	^{14}N	17.1	15.9	16.8	16.9	71
78	^{14}N	14.1	12.0	12.9	16.15	72
79	^{14}N	14.2	12.0	12.9	14.45	73
80	^{14}N	25.3	23.2	23.8	25.55	74
81	^{14}N	24.8	22.3	22.6	-25.97^{a}	75
82	^{14}N	24.8	22.0	22.0	25.4	76
83	^{14}N	27.5	25.6	26.2	26.59	75
84	^{14}N	22.3	19.7	20.2	23.8	76
85	^{14}N	24.0	21.3	21.6	27.0	77
86	^{14}N	30.0	29.8	30.1	33.3	78
87	^{14}N	31.3	31.5	31.7	32.5	79
88	^{14}N	28.8	28.7	29.1	30.5	80
89	^{14}N	30.5	30.3	30.5	32.2	80
90	^{14}N	30.3	29.6	29.8	30.7	81
91	^{14}N	30.8	30.9	31.1	31.32	82
92	^{14}N	30.5	30.7	31.0	31.14	82
93	^{14}N	28.0	28.0	28.3	31.6	81
94	^{14}N	29.9	29.5	29.7	32.2	81
95	^{14}N	30.5	30.6	30.8	30.7	81
96	^{14}N	31.5	31.8	31.9	32.6	83
97	^{14}N	28.6	28.7	29.1	30.0	83
98	^{14}N	31.2	31.5	31.6	31.6	84
99	^{14}N	31.0	30.8	30.9	31.95	80
100	^{14}N	30.3	30.7	31.0	32.0	80
101	^{14}N	31.5	31.9	32.1	31.5	84
102	^{14}N	30.3	30.8	31.0	30.85	85
103	^{14}N	30.0	30.1	30.4	31.10	85
104	^{14}N	32.1	33.0	33.1	32.60	85
105	^{14}N	32.2	32.5	32.6	32.4	80
106	^{14}N	29.0	29.2	29.6	31.0	80

[a] Experimental data have been assigned with a negative sign. [b] The assignment of the experimental hfccs has been exchanged taking into account the present theoretical calculation.

nuclei. In each figure, we represent the points corresponding to the hfcc values, the bisectrice (dotted line) and the linear fit (solid line). The results of the linear regression analysis for the three basis sets are summarized in Table 3. This table contains six well-defined columns. The first column shows the calculation level, and the rest of the columns correspond to the results of the regression analysis: intercept, slope, correlation coefficient (R^2), mean absolute deviation (MAD) and range data. The MAD only considers the absolute value, so that all deviations are converted to positive numbers, added, and then averaged. We have defined the employed MAD for our calculations in the bottom of Table 3.

From Figures 2−4, we can extract some important considerations: slopes in Figure 3 (TZVP) and Figure 4 (EPR-III) are closer to the unit value than the slope in Figure 2 (6-31G*). However, the intercept is close to zero for the 6-31G* basis

TABLE 3: Regression Analysis for Predictions of HFCCS (*G*) of ^{14}N Nuclei[a]

calculation scheme	intercept	slope	R^2	MAD[b]	range
B3LYP/6-31G*//B3LYP/6-31G*	0.58072	0.9090	0.9414	1.67	27
B3LYP/TZVP//B3LYP/6-31G*	−4.37185	1.0591	0.9209	3.53	32
B3LYP/EPR-III//B3LYP/6-31G*	−2.62692	1.0117	0.9301	2.67	30

[a] The number of points considered (*N*) is 116 in the three cases. [b] MAD (mean absolute deviation). Defined as $1/N\sum_i^N|a_{\mathrm{iso}}(\mathrm{calc}) - a_{\mathrm{iso}}(\mathrm{exp})|$.

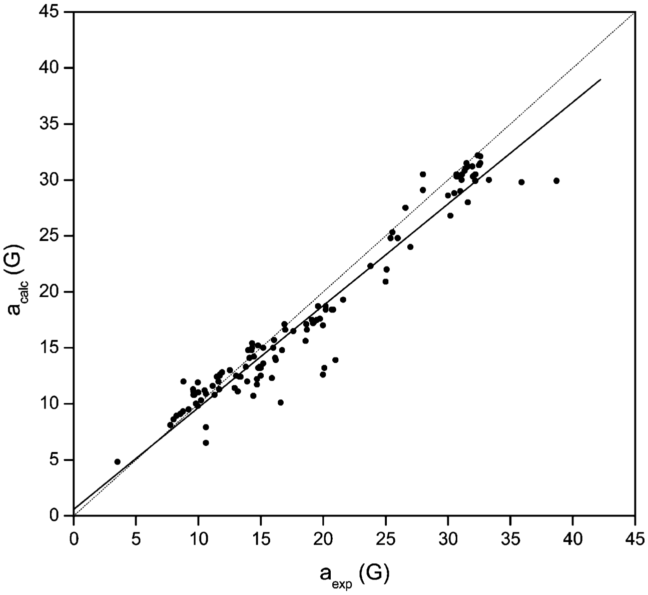

Figure 2. Plot of theoretical vs experimental a_{iso} for ^{14}N nuclei of the radicals studied, calculated at the B3LYP/6-31G*//B3LYP/6-31G* level of theory.

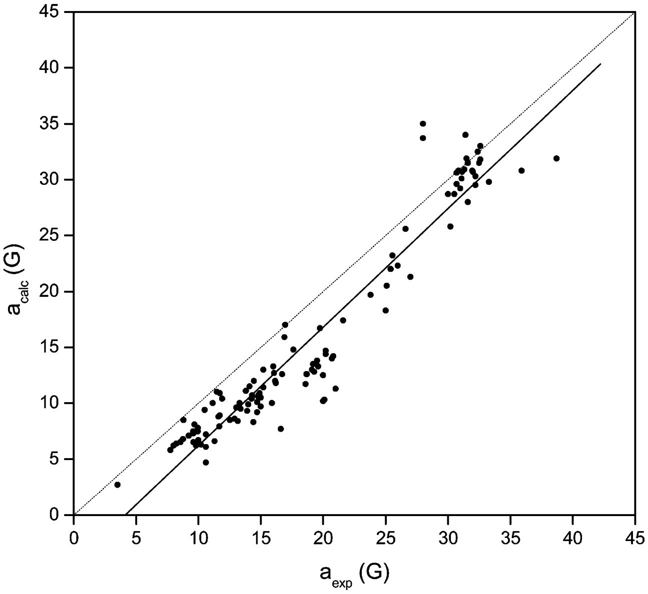

Figure 3. Plot of theoretical vs experimental a_{iso} for ^{14}N nuclei of the radicals studied, calculated at the B3LYP/TZVP//B3LYP/6-31G* level of theory.

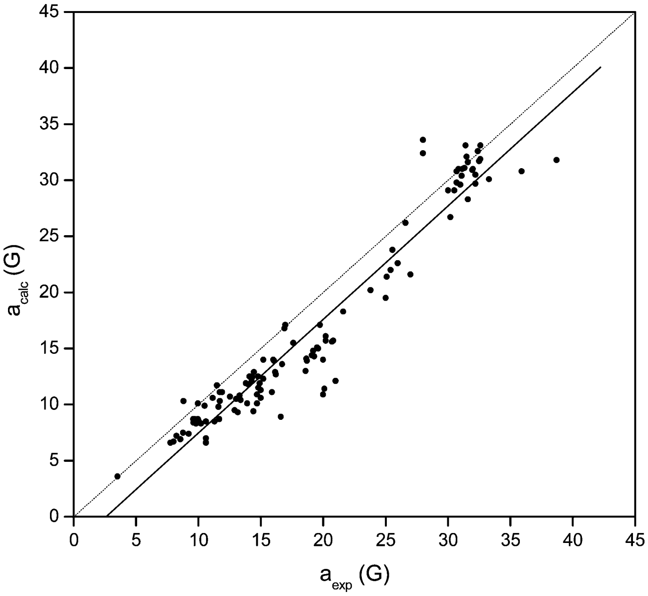

Figure 4. Plot of theoretical vs experimental a_{iso} for ^{14}N nuclei of the radicals studied, calculated at the B3LYP/EPR-III//B3LYP/6-31G* level of theory.

set, whereas it is larger and negative for the other two basis sets. The same general behavior is observed for the three basis sets: the majority of points are below the bisectrice, which indicates that experimental values are higher than theoretical ones. This outline is confirmed when Table 3 is analyzed. The range of values (27−32 G) and the correlation coefficients (0.92−0.94) are very similar for the three basis sets. The slopes of the TZVP and EPR-III basis sets are close to one, whereas the 6-31G* basis set yields ca. 0.91. However, intercepts are larger and negative for the TZVP and EPR-III basis sets, and close to zero for the smallest basis set. The values of MAD show that the fit using the 6-31G* basis set is the best one, lowest, and that the use of the TZVP basis set is not convenient to compute hfccs for N nuclei.

Conclusions

This is the most significant attempt carried out to date to compare theoretical and experimental a_{iso} values of the ^{14}N nucleus using DFT methods. For this data set of 109 nitrogen radicals, 116 experimental hfccs are available for ^{14}N nuclei. DFT provides reliable predictions of the hfccs of radicals even when not large basis sets are used. Moreover, we have observed that the kind of basis set used affects the calculation significantly.

The TZVP basis set is not good to compute hfccs for the ^{14}N nucleus, because a smaller and less computationaly demanding basis set (6-31G*) produces closer values to the experimental ones. The combination of the B3LYP functional with the 6-31G* basis set is very good for predicting nitrogen hfccs for radicals of moderate and large size. The error compensation between this incomplete basis set and this functional can also contribute to a better agreement with experimental data. The EPR-III basis set of Barone,[16] which is close to the basis set limit and, at present, the best one for calculation of hfccs of the first- and second-row nuclei, is not the most adequate for specific calculations of a_{iso} (^{14}N) of large radicals, because its high computational cost does not correspond with the little increase in the reliability of the theoretical values obtained.

The number of components of d functions plays an important role in obtaining accurate hfccs. Although the 6-31G* basis set is the smallest basis set here employed, it provides more accurate results than the other two basis sets. This could be due to the fact that it has six d functions instead of the five d functions of the TZVP and EPR-III basis sets, which is related to the fact that 6d involves an additional s function to complete the s space.

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Supporting Information Available: Table giving name, electronic ground-state symmetries and total energies for the radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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