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Validation of the B3LYP/N07D and PBE0/N07D Computational Models for the Calculation of Electronic *g*-Tensors

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Abstract: Calculations on a large set of free radicals containing atoms of the second and third row show that the computational model defined by the new N07D basis set and hybrid density functionals (B3LYP and PBE0) provides remarkably accurate *g*-tensor values at reasonable computational costs. Since in previous works it has been shown that the same computational model delivers reliable results also for structural parameters and hyperfine couplings, the route seems paved toward full a priori computation of EPR spectra of large free radicals both in vacuo and in condensed phases.

Introduction

The electronic *g*-tensor is one of the most important parameters of electronic paramagnetic resonance spectroscopy (EPR) since it contains a wealth of information about the electronic and geometrical structure of molecules with unpaired electrons. Although, theoretical approaches using density functional theory (DFT) have met considerable success for the calculation of hyperfine coupling constants,[1–8] only a limited number of systematic studies have been performed for *g*-tensors.[9–11] All magnetic tensors are, however, needed for developing an integrated computational approach to EPR spectra taking into account the proper stereoelectronic, environmental, and vibrational averaging effects.[12–14] Validation of effective methods able to compute the different building blocks of such an integrated approach for large systems is currently under way in our laboratories.[14,15]

As recently reported,[7,8] the hyperfine coupling constants calculated with PBE0 and B3LYP functionals and the new N07D basis set are in excellent agreement with experimental data; in particular our results represent significant improvements with respect to those delivered by conventional (e.g., cc-pVXZ) and purposely tailored (e.g., EPR-II and EPR-

III) basis sets.[16] So, we decided to extend this investigation to other EPR parameters and, in particular, to the *g*-tensors. In this paper we analyze the performance of the N07D basis set for a large number of radicals (92) for which reliable experimental values[17–76] are available for *g*-tensors. This set is large enough to become, in our opinion, a reference benchmark for new methods and/or basis sets.

In our previous papers[7,8] we have discussed geometrical and energetic data, together with hyperfine coupling constants for a data set including the present one, so that we will analyze in the following only *g*-tensor values.

Our aim is to show that a single model (functional/basis set) provides accurate results for second- and third-row atoms and for a large set of different radicals. In our opinion, the quality of the results and the reasonable computational cost represent a convincing proof of the utility of this basis set (N07D) in the calculation of EPR parameters.

Computational Details

All the calculations were carried out by the Gaussian03 package[77] using the B3LYP[78] and PBE0[79] hybrid density functionals with the N07D[7,8] basis set, which was recently obtained adding to a double-ζ description of valence orbitals single sets of optimized core-valence *s* (on all atoms except H), diffuse *p* (on all atoms except H), polarization (on all atoms), and diffuse *d* (on O, F, Cl atoms) functions. The

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Table 1. Theoretical and Experimental g_{iso}-Tensor (in ppm)

stucture	PBE0/EPR-III[a]	B3LYP/EPR-III[a]	PBE0/N07D	B3LYP/N07D	exp	ref
1	2.0008	2.0008	2.0010	2.0010	2.0007	17
2	2.0005	2.0005	2.0006	2.0006	2.0000	18
3	2.0002	2.0003	2.0004	2.0003	2.0003	19
4	2.0027	2.0027	2.0027	2.0027	2.0027	20
5	2.0040	2.0041	2.0039	2.0039	2.0045	21
6	2.0040	2.0040	2.0038	2.0039	2.0041	21
7	2.0033	2.0034	2.0032	2.0033	2.0031	21
8	2.0028	2.0028	2.0027	2.0028	2.0028	22
9	2.0042	2.0042	2.0041	2.0041	2.0036	23
10	2.0027	2.0027	2.0026	2.0027	2.0027	20
11	2.0028	2.0028	2.0027	2.0028	2.0028	24
12	2.0029	2.0029	2.0028	2.0028	2.0026	25
13	2.0045	2.0047	2.0044	2.0045	2.0049	26
14	2.0046	2.0047	2.0044	2.0045	2.0047	27
15	2.0044	2.0045	2.0043	2.0044	2.0045	28
16	2.0043	2.0044	2.0041	2.0042	2.0043	29
17	2.0046	2.0047	2.0044	2.0045	2.0045	29
18	2.0044	2.0045	2.0042	2.0043	2.0045	30
19	2.0034	2.0035	2.0033	2.0034	2.0032	31
20	2.0036	2.0037	2.0035	2.0036	2.0035	29
21	2.0037	2.0038	2.0036	2.0037	2.0036	32
22	2.0038	2.0039	2.0037	2.0037	2.0035	33
23	2.0039	2.0039	2.0037	2.0038	2.0037	29
24	2.0028	2.0028	2.0028	2.0028	2.0028	34
25	2.0028	2.0029	2.0028	2.0028	2.0029	22
26	2.0038	2.0039	2.0037	2.0037	2.0038	35
27	2.0038	2.0039	2.0037	2.0037	2.0038	35
28	2.0039	2.0039	2.0037	2.0038	2.0038	35
29	2.0038	2.0039	2.0037	2.0037	2.0036	36
30	2.0035	2.0035	2.0034	2.0034	2.0034	37
31	2.0002	2.0002	2.0004	2.0004	2.0024	38
32	2.0036	2.0034	2.0039	2.0039	2.0042	39
33	2.0007	2.0007	2.0008	2.0008	2.0024	38
34	2.0036	2.0035	2.0037	2.0037	2.0042	39
35	2.0036	2.0035	2.0037	2.0037	2.0042	39
36	2.0034	2.0033	2.0035	2.0035	2.0039	40
37	2.0019	2.0018	2.0019	2.0019	2.0020	38
38	2.0056	2.0057	2.0053	2.0055	2.0050	41
39	2.0057	2.0058	2.0054	2.0056	2.0050	41
40	2.0057	2.0058	2.0054	2.0056	2.0049	42
41	2.0041	2.0042	2.0039	2.0041	2.0028	34
42	2.0046	2.0047	2.0045	2.0047	2.0028	43
43	2.0047	2.0048	2.0045	2.0048	2.0057	44
44	2.0050	2.0052	2.0048	2.0052	2.0060	44
45	2.0048	2.0050	2.0047	2.0050	2.0055	45
46	2.0042	2.0043	2.0041	2.0043	2.0062	46
47	2.0050	2.0052	2.0048	2.0052	2.0063	47
48	2.0050	2.0051	2.0048	2.0049	2.0047	48
49	2.0049	2.0051	2.0048	2.0049	2.0047	48
50	2.0068	2.0069	2.0064	2.0066	2.0057	37
51	2.0063	2.0064	2.0060	2.0061	2.0055	49
52	2.0063	2.0063	2.0059	2.0060	2.0054	49
53	2.0062	2.0063	2.0058	2.0060	2.0059	45
54	2.0063	2.0064	2.0060	2.0061	2.0060	50
55	2.0063	2.0064	2.0060	2.0061	2.0059	51
56	2.0010	2.0010	2.0011	2.0011	2.0013	17
57	2.0091	2.0091	2.0085	2.0089	2.0041	52
58	2.0080	2.0084	2.0076	2.0081	2.0093	17
59	1.9993	1.9993	1.9995	1.9994	2.0002	18
60	2.0016	2.0016	2.0017	2.0017	2.0010	53
61			2.0003	2.0002	2.0020	54
62			2.0008	2.0009	2.0036	55
63			2.0043	2.0046	2.0032	56
64			2.0017	2.0020	2.0009	56
65			2.0024	2.0027	2.0017	57
66			2.0037	2.0037	2.0032	58
67			2.0036	2.0036	2.0031	59
68			2.0034	2.0035	2.0032	20
69			2.0016	2.0017	2.0012	60
70			2.0033	2.0033	2.0030	59
71			2.0053	2.0054	2.0050	59

Table 1. Continued

stucture	PBE0/EPR-III[a]	B3LYP/EPR-III[a]	PBE0/N07D	B3LYP/N07D	exp	ref
72			2.0087	2.0089	2.0087	61
73			2.0116	2.0118	2.0130	62
74			2.0166	2.0200	2.0250	56
75			2.0028	2.0028	2.0030	63
76			2.0057	2.0059	2.0050	64
77			2.0065	2.0067	2.0059	65
78			2.0032	2.0031	2.0035	62
79			2.0044	2.0048	2.0030	66
80			2.0119	2.0121	2.0123	67
81			2.0020	2.0074	2.0070	68
82			2.0063	2.0063	2.0055	69
83			2.0044	2.0042	2.0058	68
84			2.0068	2.0070	2.0071	70
85			2.0068	2.0073	2.0045	71
86			2.0088	2.0088	2.0084	72
87			2.0086	2.0086	2.0079	72
88			2.0105	2.0105	2.0094	73
89			2.0066	2.0065	2.0061	74
90			2.0085	2.0084	2.0085	75
91			2.0076	2.0075	2.0071	72
92			2.0086	2.0086	2.0081	76

[a] Single point calculations on geometries optimized at the PBE0/N07D level.

Table 2. Data Analysis for Structures with Second-Row Atoms[a]

	PBE0/EPR-III[b]	B3LYP/EPR-III[b]	PBE0/N07D	B3LYP/N07D	exp
60 molecules					
MAD	0.0006	0.0006	0.0005	0.0005	
max absolute error	0.0050	0.0050	0.0044	0.0048	
R2	0.7303	0.7447	0.7403	0.7505	
intercept	0.1046	0.0440	0.2439	0.1470	
slope	0.9478	0.9781	0.8782	0.9266	
max	2.0091	2.0091	2.0085	2.0089	2.0093
min	1.9993	1.9993	1.9995	1.9994	2.0000

[a] MAD (mean absolute deviation in Gauss) = $\Sigma g_{calc} - g_{exp}/N$. [b] Single point calculations on geometries optimized at the PBE0/N07D level.

inner electrons of second- and third-row atoms are described by the 6G basis set.[80]

Geometry optimizations and evaluations of harmonic frequencies have been performed in the gas-phase using analytical gradients and Hessians.

The gyromagnetic tensor can be written as $g = g_e \mathbf{1}_3 + \Delta g_{RM} + \Delta g_G + \Delta g_{OZ/SOC}$ where g_e is the free-electron value (2.0023193). Computation of the relativistic mass (RM) and gauge (G) corrections is quite straightforward because they are first-order contributions.[81] The last term arises from the coupling of the orbital Zeeman (OZ) and the spin−orbit coupling (SOC) operator. The OZ contribution is computed using the gauge-including atomic orbital (GIAO) approach,[82] whereas for light atoms the two electron SOC operator can be reliably approximated by a one electron operator involving adjusted effective nuclear charges.[83] Although those charges were optimized for MCSCF wave functions, a number of test computations showed that they are nearly optimal for DFT computations too. Upon complete averaging by rotational motions, only the isotropic part of the g tensor survives, which is given by $g_{iso} = \frac{1}{3} \text{Tr}(g)$. Of course, the corresponding shift from the free electron value is $\Delta g_{iso} = g_{iso} - g_e$. All the results will be given in the following as g-tensor values.

Results and Discussion

The N07D basis set[7,8] has been assessed by comparison with EPR-III[84] basis set for the g-tensors. Our results are collected

Table 3. Data Analysis for Structures with Second- and Third-Row Atoms[a]

	PBE0/N07D	B3LYP/N07D	exp
92 molecules			
MAD	0.0006	0.0006	
max absolute error	0.0050	0.0048	
R2	0.8159	0.8525	
intercept	0.1369	0.0595	
slope	0.9317	0.9704	
max	2.0120	2.0121	2.0130
min	1.9995	1.9994	2.0000

[a] MAD (mean absolute deviation in Gauss) = $\Sigma g_{calc} - g_{exp}/N$.

in Tables 2−4 and compared with experimental results. A variety of molecules containing atoms from the second and third row of the periodic table have been studied. The selected set of 92 radicals (shown in Figure a-b) includes neutral, cationic, anionic, localized, and conjugated species. Before considering detailed results, we recall that the EPR-III[84] basis set is available only for hydrogen and second-row atoms (Tables 1 and 2).

A statistical analysis has been performed for the whole data set. In detail, we report the number of data (N), mean absolute deviation (MAD), and data range between calculated and experimental values. Next we give the correlation coefficient (R^2), slope, and intercept of the least-squares line. The MAD is an absolute value, so that all deviations are converted to positive numbers, added, and then averaged.

Table 4. Calculated and Experimental *g*-Tensors (ppm) of Glycine Radical in Aqueous Solution

	exp		PBE0/EPR-III		PBE0/N07D		B3LYP/EPR-III		B3LYP/N07D	
	cis	trans	cis	trans	cis	trans	cis	trans	cis	trans
Δg_{xx}			2503.3	2620.4	2276.2	2388.2	2593.1	2702.6	2362.9	2468.5
Δg_{yy}			1386.3	1994.9	1259.1	1814.9	1437.8	2059.2	1295.9	1857.5
Δg_{zz}			−177.4	−175.7	−171.9	−172.0	−179.4	−177.6	−175.3	−173.2
g_{iso}	2.00340	2.00340	2.00356	2.00380	2.00344	2.00366	2.00360	2.00385	2.00348	2.00370
					with $\Delta_{PCM-gas}$					
Δg_{xx}			2586.3	2565.7	2359.2	2333.5	2676.1	2647.9	2445.9	2413.8
Δg_{yy}			1413.7	1928.2	1286.5	1748.2	1465.2	1992.5	1323.3	1790.8
Δg_{zz}			−191.8	−187.1	−186.3	−183.4	−193.8	−189.0	−189.7	−184.6
g_{iso}	2.00340	2.00340	2.00360	2.00375	2.00348	2.00361	2.00364	2.00380	2.00352	2.00365
					with $\Delta_{GLOB/ADMP-gas}$					
g_{iso}	2.00340	2.00340	2.00356	2.00371	2.00344	2.00357	2.00360	2.00376	2.00348	2.00361

Table 5. Calculated and Experimental *g*-Tensors (ppm) of Glycyl Radical in Solution (Water)[a]

	$\Delta g_{298}°$	Δg_{solv}	Δg_{gas}N07D[b]	Δg_{gas} EPR-III[b]	Δg_{gas} EPR-III[c]
Δg_{xx}	−26.4	320.9	2190.1	2423.5	2363.9
Δg_{yy}	−28.9	−489.4	1402.1	1546.4	1524.9
Δg_{zz}	4.4	−5.4	−164.9	−170.3	−173.3

	Best estimate			exp[d]				
	N07D[b]	EPR-III[b]	EPR-III[c]	RNR	RNR	PFI	BSS	N-acetyl glycyl
Δg_{xx}	2484.6	2718.0	2658.4	1900	2000	2400	2200	2200/1900
Δg_{yy}	883.8	1028.1	1006.6	1000	1000	1600	1300	800/900
Δg_{zz}	−165.9	−171.3	−174.3	0	0	200	−100	−300/400

[a] The experimental data are given with an error of ±400 ppm. [b] Geometry optimized at the PBE0/N07D level. [c] Geometry optimized at the PBE0/6−31+G(d,p) level. [d] From ref 11a.

Moreover, regression analysis represents, in our opinion, the simplest and most useful approach for an unbiased comparison between large sets of computed and experimental values.

We analyze the data in two steps. In the first one, we consider the 60 structures (Table 2) containing second-row atoms (Figure a) and compare the results obtained with the new basis set with both experimental and theoretical (EPR-III) data; next, we compare for all structures, i.e. including those containing also third-row atoms (Table 3), the *g*-tensors values calculated with the N07D basis set to experimental data. In general terms our calculations (Tables 1−3) show that the density functional (PBE0 vs B3LYP) has a marginal effect on the magnitude of the *g*-tensor (Tables 1−3). Thus, the performance of the basis sets has been evaluated using the PBE0 and B3LYP functionals and compared in Tables 2 and 3 (MADs). The N07D results (Table 2) are slightly better (0.0005 vs 0.0006 ppm for both functionals) than the EPR-III results in terms of MADs, and the corresponding computational cost is significantly lower. As a matter of fact, the difference between N07D basis sets for PBE0 and B3LYP functional involves only tight s functions, which have a negligible effect on valence properties like *g*-tensors. In the same vein, 6−31+G(d,p) results should be comparable for *g*-tensors, but this is not the case for structures and hyperfine parameters. The strength of the N07D basis set is the contemporary reproduction of all those properties at a reasonable cost: this is especially significant for second-order properties (like *g*-tensors) whose computation has a scaling with the number of basis functions significantly worse than that of first order properties (like hyperfine properties). For

instance, the number of contracted functions for a second-row atom is 19 and 40 for N07D and EPR-III basis sets, respectively. The N07D basis set is thus characterized by an excellent accuracy/time ratio: this is a crucial result for our aim of using a unique functional/basis set model for the calculation of geometric, electronic, and magnetic properties of free radicals.

The performances of the B3LYP/N07D and PBE0/N07D models for a typical problem involving at the same time stereoelectronic, vibrational, and environmental effects can be judged by the results reported in Tables 4 and 5 for the glycine[13c,15a] and glycyl[10b] radicals (Figure 2) in condensed phases. Let us start from the glycine radical. In Table 4 are reported the principal components of the *g*-tensors (δg_{xx}, δg_{yy}, and δg_{zz}) and the g_{iso} values carried out using both functionals (PBE0 and B3LYP) and basis sets (EPR-III and N07D) together with the g_{iso} value measured in aqueous solution (2.00340 ± 0.00005). Since the *g*-tensors computed for the minimum energy structure in vacuum are significantly tuned by both intramolecular vibrations and by solvent librations, the reported results are obtained by averaging over 100 frames extracted at regular time steps from the ab initio dynamics described in ref 15a. As shown, the *g*-tensors are sensitive to the conformation of the radical, e.g. the *g*-tensors of GlyR[cis] and GlyR[trans] are significantly different (Table 4). In particular, the results obtained with the N07D basis set for GlyR[cis] are in remarkable agreement with experiment, confirming the prevalence of this isomer in aqueous solution suggested by direct energetic evaluations.

In Table 5, we compare our results for the glycyl radical with the theoretical ones issuing from PBE0/EPR-III com-
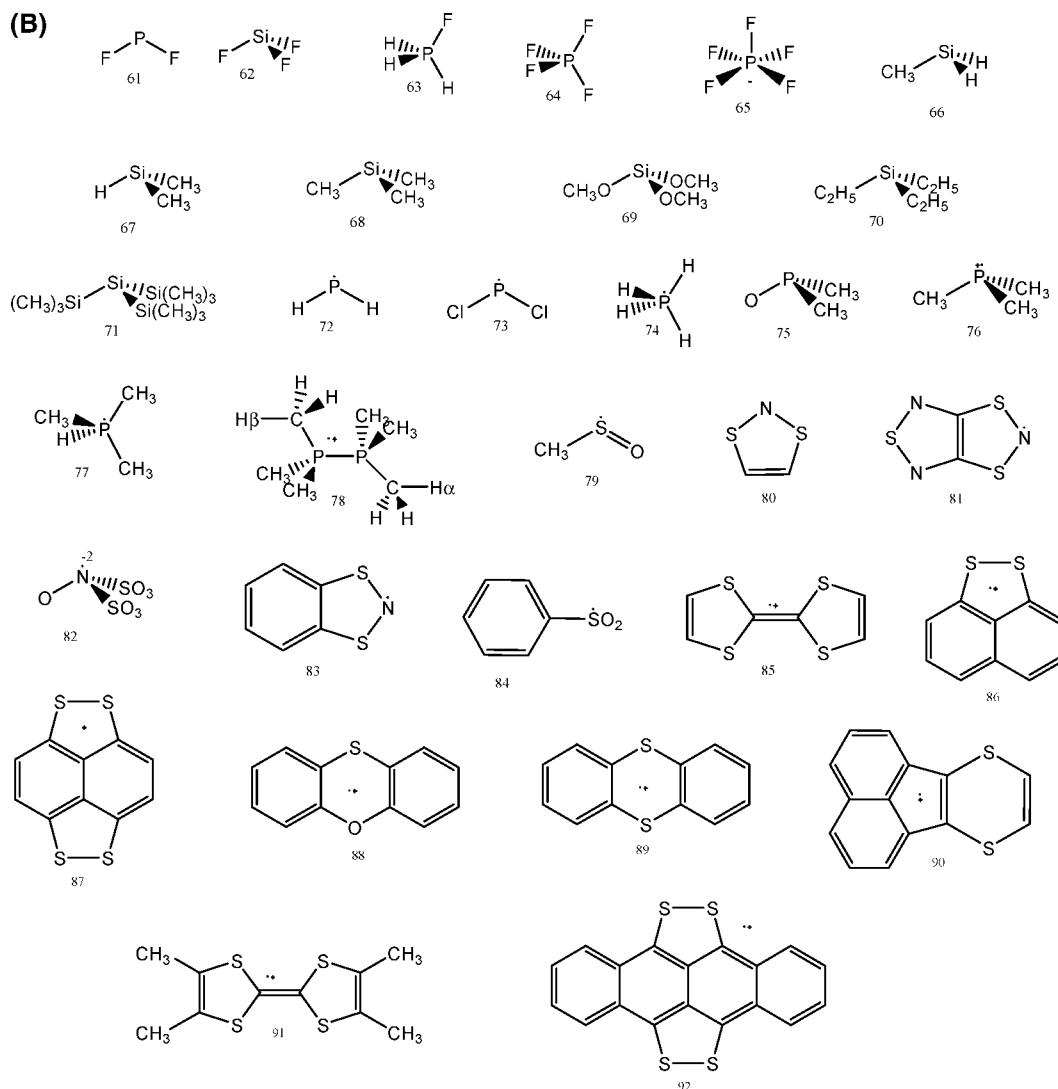
(A)

(B)
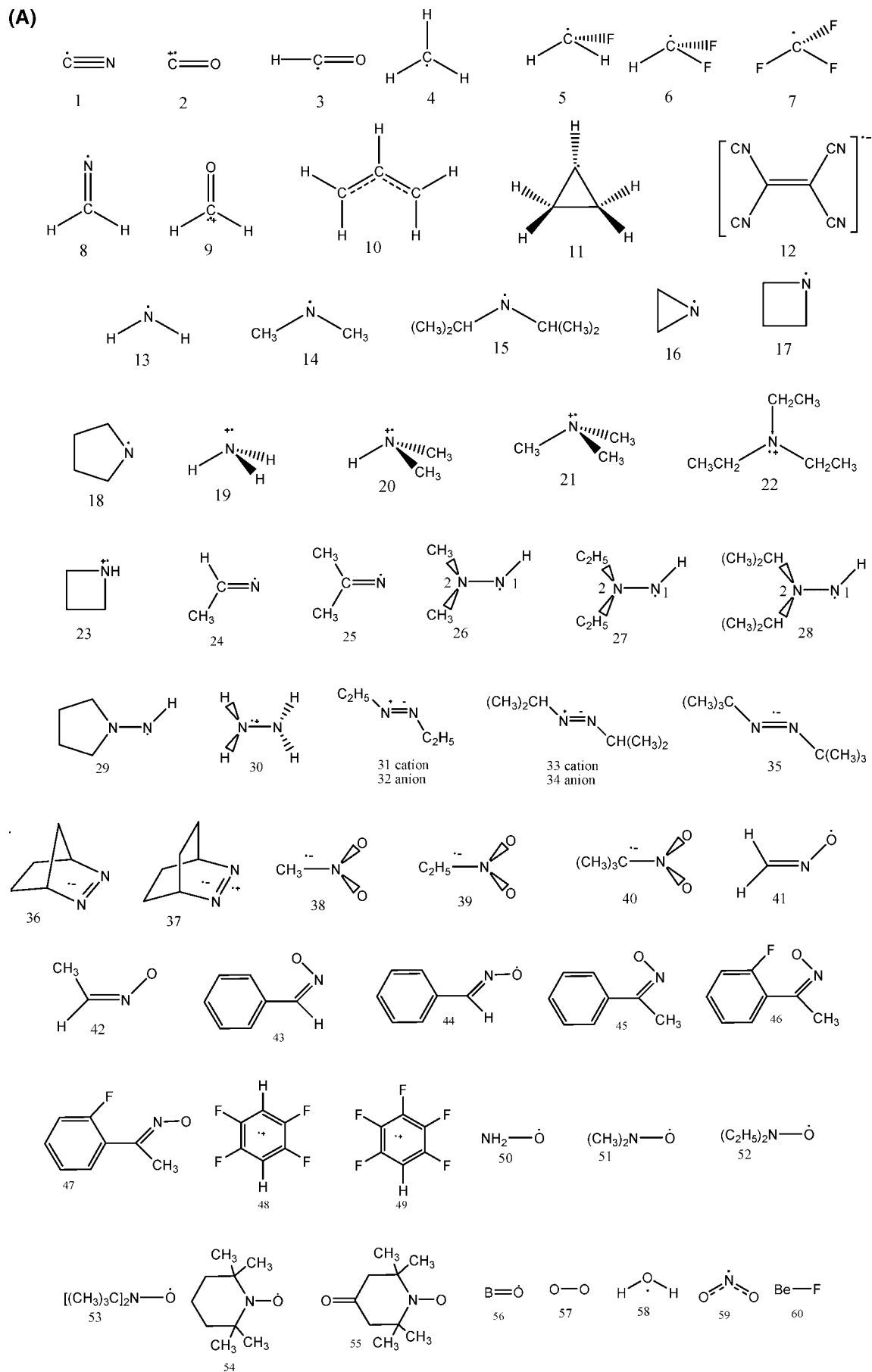
Figure 1. Structures of the radicals studied with (a) second-row atoms and (b) third-row atoms.
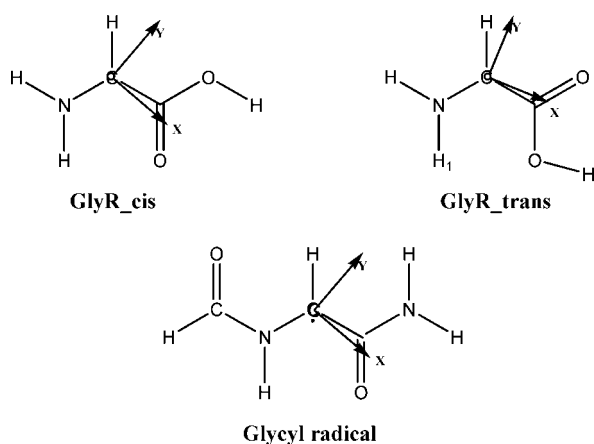

Figure 2. Structures of glycine and glycyl radicals. The orientations of the principal axes of the *g*-tensor are also shown.

putations and with experimental data obtained for different enzymes and for N-acetylglycyl radical. In general, the *g*-tensors calculated with the N07D basis set are slightly smaller than those obtained with EPR-III basis set. Moreover, as reported in previous papers, the *g*-tensors are affected by both direct and indirect solvent effects as well as by intramolecular motions. Comparison with experiment confirms the remarkable performances of B3LYP/N07D and PBE0/N07D computational models when taking into account the proper dynamical and environmental effects.

Concluding Remarks

The present paper reports the results of a systematic computational study devoted to the calculation of *g*-tensor values using the new N07D basis set. The PBE0/N07D and B3LYP/N07D results for a representative set of organic free radicals seem accurate enough to allow for quantitative studies. This finding together with the computational efficiency of the approach suggest that we dispose of a quite powerful tool for the study of free radicals, especially taking into account that the same density functional and basis set can be used for different properties and for second- and third-row atoms. Furthermore, the availability of effective discrete/continuum solvent models and of different dynamical approaches, together with the reduced dimensions of the N07D basis set, allow for performing comprehensive analyses aimed at evaluating the roles of stereoelectronic, vibrational, and environmental effects in determining the overall

properties of large flexible radicals of current biological and/ or technological interest.

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