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Calculations of Isotropic Hyperfine Coupling Constants of Organic Radicals. An Evaluation of Semiempirical, Hartree–Fock, and Density Functional Methods

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The geometries and the isotropic hyperfine coupling constants of 17 different organic radicals and radical ions were calculated with the use of semiempirical, Hartree–Fock, and density functional methods. A good agreement between the experimental and the theoretical data was found when the geometry of the radical was optimized with density functional methods or the UHF/3-21G* *ab initio* method, and the Fermi interaction was calculated with the density functionals BLYP/6-31G* or B3LYP/6-31G* at the unrestricted level of theory. This statement holds for all types of radicals studied, *i.e.* neutral radicals (allyl, bicyclo[1.1.1]pent-1-yl, cubyl, 1,2,3,4,5,6-hexafluorocyclohexadienyl, 2-methyldihydrofuran-4-yl, •PH(CH₃)₃), radical cations (norbornadiene, quadricyclane, 1,8-dimethylnaphthalene, acenaphthene, tetramethylhydrazine, 1,2-di(*tert*-butyl)-1,2-dimethylhydrazine, 1,5-diazabicyclo[3.3.0]octane, 2,3-dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene), and radical anions (naphthalene, 1,8-dimethylnaphthalene, acenaphthene).

1. Introduction

ESR spectroscopy is an important method for the direct observation of radicals generated from organic molecules in solution.¹ The hyperfine coupling constants of magnetic nuclei (a_i where i = type of nucleus, *e.g.* ¹H, ¹³C, ¹⁴N) and the line pattern of an ESR spectrum contain the information about the structure and geometry of such radicals. The experimental data have to be compared with their theoretical counterparts to gain insight into the particular properties of the detected radical.

The a_i arise from the Fermi contact interaction between the unpaired electron and the nucleus.^{1,2} This is described in eq 1.

$$a_i = (2/3)g_e g_N \mu_B \mu_N \mu_0 (1/ha_0^3) Q(0) \quad (1)$$

There, a_i is the isotropic hyperfine coupling (in Hz) of a nucleus i , g_e and g_N are the electron and nuclear g factors, μ_B and μ_N are the Bohr and the nuclear magneton, respectively, μ_0 is the vacuum permeability, h is the Planck constant, a_0 is the Bohr radius, and $Q(0)$ is the spin density at the nucleus i . Whereas $g_e g_N \mu_B \mu_N \mu_0 (1/ha_0^3)$ is constant for a specific nucleus, $Q(0)$ has to be determined from quantum theoretical calculations.

The interaction between the nucleus and the unpaired electron predominately depends upon the s character of the singly occupied orbital (SOMO) at the particular atom. Thus, it is necessary to have representative geometry parameters for the radical and a wave function that describes the area at the nucleus in detail.

The methods used to predict a_i range from the simplistic Hückel model without geometry optimization^{3,4} to rather complex *ab initio* techniques.⁵

For planar delocalized organic π radical ions with nondegenerate orbitals Hückel–McConnell⁶ calculations give a_i close

to the experimental ones;⁴ structural or geometrical features of these radicals are obviously not predictable.⁷ For π radicals also the PPP⁸ method was reported to give feasible a_i values.⁹

The geometry of organic radicals is frequently optimized by semiempirical calculations¹⁰ as well as by *ab initio* methods.¹¹ The a_i values are then determined by Pople's INDO¹² or Nelsen's version¹³ of the unrestricted AM1 method.¹⁴

Last but not least, high-level *ab initio* methods have been used to calculate the Fermi contact interaction of small radicals.^{5,15}

The above methods have been predominately developed to investigate molecular geometries and energies, *i.e.* properties that are related to the outer shells. In contrast the Fermi contact interaction responsible for the a_i is a local property of the nucleus. Therefore certain factors have to be considered for the calculation of isotropic hyperfine data. In particular, it is important to consider electron correlation. This was achieved by the incorporation of configuration interaction techniques into the calculations of a_i .^{15,16} Further developments include the use of multiconfiguration self-consistent field (MCSCF)¹⁷ or multireference CI.¹⁸ A compilation of methods is given by Chipman,^{16c} and a comparison of some of these methods is given by Huang et al. and Malkin et al.^{18,19}

The latter highly sophisticated methods are at the moment only practicable for a small number of atoms. The large molecules that are of interest to organic chemists afford extensive CPU times.

In recent publications it has been shown that the density functional theory (DFT) formalism²⁰ can be used very efficiently to predict the hyperfine coupling constants for radicals comprising up to four heavy atoms.^{16a,18,21}

The DFT method requires considerably less computational time than sophisticated *ab initio* techniques. Therefore we have tested several different procedures for the calculation of the

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geometry and the isotropic hyperfine coupling constants of organic radicals and radical ions.

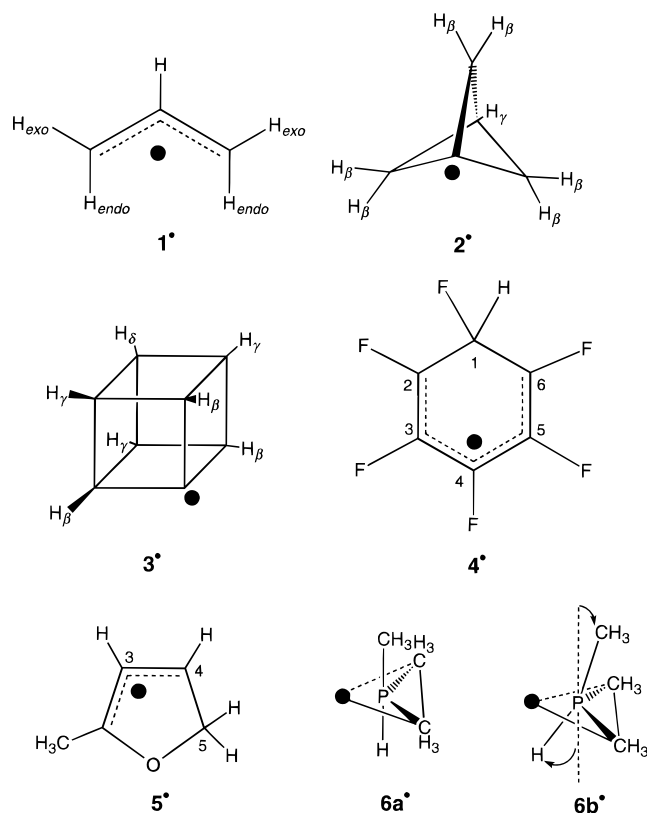
The molecules studied were chosen with respect to the following criteria: (i) we wanted to cover a broad range of compounds, *i.e.*, hydrocarbons, π systems, rigid and flexible molecules, heteroatomic compounds; (ii) the a_i should be known from experiment. In addition, we used generally accessible programs.

The aim of this investigation is to test whether there is a general computational protocol that leads to good agreement with experimental data and thus provides insight into the nature of organic radicals and radical ions. Therefore, in this paper, we will not discuss the peculiarities of the individual radicals, as their features are already well described, but concentrate on the agreement between calculated and experimental data.

2. Choice of Molecules

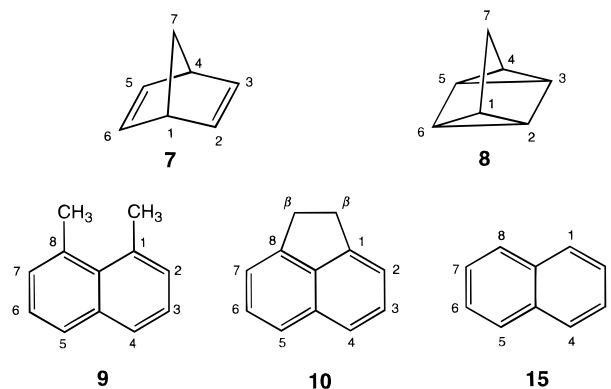
To survey the utility of computational methods for neutral radicals, radical cations, and radical anions, the following molecules were selected as prototypes.

The allyl radical (**1**[•])²² is the simplest delocalized neutral radical and the spectra are well documented. The polycyclic skeletons of bicyclo[1.1.1]pentane and cubane give radicals **2**[•]²³ and **3**[•],²⁴ respectively, with considerable s character caused by the pyramidalized radical centers in the strained skeletons. In the 1,2,3,4,5,6-hexafluorocyclohexadienyl radical,²⁵ **4**[•], the F atoms effect a slight deviation of the π radical centers from planarity. Moreover, the calculated a_i of non-hydrogen β and γ substituents can be compared with the experimental counterparts. Radical **5**[•] (2-methyldihydrofuran-4-yl) is an allyl radical derived from furan and is of interest as a model intermediate in the 4'-DNA radical cleavage.²⁶ With the $\cdot\text{PH}(\text{CH}_3)_3$ radical²⁷ **6** the quality of the calculations concerning second-row main group elements will be inspected.

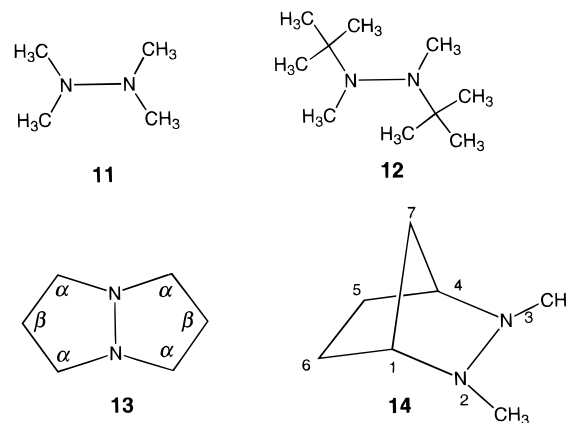


The radical cations are represented by the recently characterized isomers of norbornadiene (**7**)²⁸ and quadricyclane (**8**).²⁹

For the latter, two differing sets of a_H have been reported. The "classical" π systems 1,8-dimethylnaphthalene (**9**)³⁰ with the freely rotating methyl groups (β protons) and acenaphthene (**10**),³¹ in which the five-ring annelation leads to the build up



of peri strain,³² have also been included. The a_i of analogous systems are even today calculated with Hückel-related techniques because semiempirical treatment gives very poor agreement with the experimental a_i (see Tables 9, 10, 15–17). A great deal of experimental and calculated data are available for hydrazine-type radical cations. The ¹⁴N hyperfine coupling constant, a_N , is very characteristic for the structure of these radicals; four such compounds with differing geometries were included in this study. The flexible tetramethylhydrazine (**11**)³³ allows fast dynamics of the NR₃ moieties; these are restricted by the bulky *tert*-butyl groups in **12**³³ and are gradually more hindered in the polycyclic systems **13**³³ and **14**.³³ In the strained derivative **14** the nitrogens are not able to adopt a planar geometry upon electron loss.



The variety of radical anions in the literature is by far more limited. Generally organic radical anions are generated from rather extended, predominately planar delocalized π systems (see, for example, Davies and Gescheidt³⁴). Thus, we have selected the simple naphthalene derivatives **9** and **10** together with the parent compound (**15**).³⁵ For the radical anions of **15**, **9**, and **10**, the influence of alkyl substitution and of peri strain on the spin distribution will be examined.

3. Computational Procedure

3.1. Technical Details. The AM1¹⁴ optimizations were carried out with MOPAC 6.00.³⁶ The *ab initio* and density functional calculations were performed using GAUSSIAN 94.³⁷ All these calculations were performed on IBM RS/6000 or HP 735 workstations. A modified version of INDO¹² was employed for calculating the a_H ,³⁸ this was done on a VAX 7000–620.

TABLE 1: Comparison of Experimental and Calculated a_H of the Allyl Radical, 1^\bullet

calc of geom/spin (single point (Fermi))/geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(\text{endo}, 2 \text{ H})/\text{mT}$	$a_H(\text{exo}, 2 \text{ H})/\text{mT}$	$a_H(2)/\text{mT}$
exptl ²²		1.390	1.481	0.406
AM1//AM1	0.930/0.756	-1.531	-1.569	0.977
B3LYP/6-31G*//AM1	0.782/0.750	-1.621	-1.684	0.540
B3LYP/6-31G*//UHF/3-21G*	0.783/0.750	-1.597	-1.662	0.530
BLYP/6-31G*//AM1	0.765/0.750	-1.433	-1.490	0.354
BLYP/6-31G*//UHF/3-21G*	0.766/0.750	-1.412	-1.471	0.346
INDO//UHF/3-21G*		-1.455	-1.439	0.725
B3LYP/6-31G*//B3LYP/6-31G*	0.782/0.750	-1.581	-1.652	0.497
BLYP/6-31G*//BLYP/6-31G*	0.766/0.750	-1.405	-1.469	0.321

TABLE 2: Comparison of Experimental and Calculated a_H of the Bicyclo[1.1.1]pent-1-yl Radical, 2^\bullet

calc of geom/spin (single point (Fermi))/geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(\beta, 6 \text{ H})/\text{mT}$	$a_H(\gamma, 1 \text{ H})/\text{mT}$
exptl ²³		0.12	6.96
AM1//AM1	0.756/0.750	0.03	2.54
B3LYP/6-31G*//AM1	0.752/0.750	-0.12	6.24
B3LYP/6-31G*//UHF/STO-3G	0.752/0.750	-0.10	5.73
B3LYP/6-31G*//UHF/3-21G*	0.752/0.750	-0.11	5.46
BLYP/6-31G*//AM1	0.752/0.750	-0.10	6.42
BLYP/6-31G*//UHF/STO-3G	0.752/0.750	-0.09	5.97
BLYP/6-31G*//UHF/3-21G*	0.752/0.750	-0.10	5.68
INDO//UHF/3-21G*		0.08	6.12
B3LYP/6-31G*//B3LYP/6-31G*	0.752/0.750	-0.11	6.36
BLYP/6-31G*//BLYP/6-31G*	0.752/0.750	-0.11	6.61

3.2. Methods and Proceedings. The following methods were used for geometry optimizations: AM1, Hartree Fock with STO-3G, and 3-21G* basis sets, and DFT using correlation functionals of Lee, Yang, and Parr with the exchange functional by Becke (BLYP)³⁹ as well as Becke's three-parameter hybrid method with HF, using the LYP functional (B3LYP)⁴⁰ with a 6-31G* basis set. The Fermi contacts $Q(0)$ were calculated for INDO, AM1, and the above two DFT methods. The two DFT methods were chosen because they have been shown to provide a_H values agreeing closely with the experimental data.⁴¹ All techniques were applied at the unrestricted level of theory.

To distinguish between effects originating in differing geometries and the method of the calculation of the Fermi contact, we have followed two strategies. First, we optimized the geometry of each compound with AM1, UHF/STO-3G, and UHF/3-21G*. Then, on the basis of these geometries, DFT single-point calculations were performed. From these the Fermi contact interactions were calculated. Finally they were transformed to the hyperfine coupling constants with the use of the relationship given in eq 1. The calculated hyperfine coupling constants refer to the $Q(0)$ values after spin annihilation.

In our experience it turned out that the geometry optimizations for aromatic systems with STO-3G in many cases required longer CPU times than with the 3-21G* basis set. For this reason we did not rigorously pursue the geometry optimization with the minimal basis set.

In addition, both the geometry optimization and the Fermi contact calculation were computed with BLYP/6-31G* and B3LYP/6-31G*. These DFT geometry optimizations require at least an order of magnitude more CPU time than UHF/3-21G* with the use of GAUSSIAN 94.

UMP2(full)/6-31G*//UHF/3-21G* calculations were also tested in some cases to determine their usefulness in obtaining reasonable Fermi contacts. Generally the results by this method did not justify the significant expense in CPU time (see Conclusion and Figure 2).

4. Results and Discussion

4.1. Neutral Radicals. For the allyl radical 1^\bullet (Table 1), all theoretical methods show a fair correlation with the experimental results. The predictions for the a_H of *exo* and *endo* protons

deviate only up to *ca.* 0.25 mT, assigning the lower value to the *endo* protons. The $a_H(2)$ is predicted best by the DFT methods based on the UHF/3-21G* or DFT geometries.

Owing to the rigid molecular frameworks of 2^\bullet and 3^\bullet , the differences in the AM1-, *ab initio*-, or DFT-calculated geometries are only marginal. The a_H assigned to the six equivalent β -protons and to the single bridgehead proton of 2^\bullet differ by a factor of 60.²³ The theoretical values reproduce this difference quite well. However, AM1 gives much too low a_H for both types of protons. When the AM1 geometry is used for the single-point calculation of the Fermi contact with the density functionals, the agreement with the experimental data is considerably improved; this also holds for the *ab initio* geometries (Table 2). It is noteworthy that the INDO//UHF/3-21G* method also yields matching results. The predictions of the a_H in the cubyl radical 3^\bullet are less straightforward.²⁴ The semiempirical methods predict very differing a_H (Table 3). The DFT-determined a_H based on the AM1 or UHF geometries show a much better fit to the ESR spectral data, but the difference between $a_H(\gamma)$ and $a_H(\delta)$ of 0.19 mT is not reproduced. A closer correlation is achieved when a DFT geometry is employed (Table 3).

When heteroatoms are present in the neutral radicals as in the 1,2,3,4,5,6-hexafluorocyclohexadienyl radical, 4^\bullet ,²⁵ and trimethylphosphoranyl radical, 6^\bullet ,²⁷ AM1 and INDO cannot be used because the corresponding proportionality factors for the conversion of the spin density into the coupling constant are not available. The INDO program is limited to first-row elements. The DFT single points on UHF/3-21G* geometries or DFT-optimized geometries of 4^\bullet give reasonable agreement with the experimental values (Table 4). In the case of 5^\bullet ,²⁶ all geometry optimization procedures yield very similar results. This is exemplified by the conformity of the DFT-calculated hyperfine data (Table 5). On the other hand, AM1 and UHF/3-21G* optimizations give significantly different geometries with 6^\bullet . Whereas the P atom is pyramidalized with AM1 (**6b**), the *ab initio* as well as the DFT methods predict a trigonal-bipyramidal arrangement around the P atom (**6a**). Two methyl groups and the P lone pair (with the unpaired electron) define the trigonal plane, whereas the H atom and one methyl group occupy the axial positions. With the use of the geometry obtained by the

TABLE 3: Comparison of Experimental and Calculated a_H of the Cubyl Radical, 3[•]

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(\beta, 3 \text{ H})/\text{mT}$	$a_H(\gamma, 3 \text{ H})/\text{mT}$	$a_H(\delta)/\text{mT}$
exptl ²⁴		1.24	0.82	0.63
AM1//AM1	0.758/0.750	0.13	0.29	0.29
B3LYP/6-31G*//AM1	0.753/0.750	1.12	0.69	0.59
B3LYP/6-31G*//UHF/STO-3G	0.753/0.750	1.07	0.67	0.66
B3LYP/6-31G*//UHF/3-21G*	0.753/0.750	0.98	0.66	0.61
BLYP/6-31G*//AM1	0.752/0.750	1.19	0.73	0.74
BLYP/6-31G*//UHF/STO-3G	0.752/0.750	1.14	0.71	0.83
BLYP/6-31G*//UHF/3-21G*	0.752/0.750	1.04	0.69	0.76
INDO//UHF/3-21G*		0.92	0.83	1.01
B3LYP/6-31G*//B3LYP/6-31G*	0.753/0.750	1.17	0.74	0.57
BLYP/6-31G*//BLYP/6-31G*	0.752/0.750	1.16	0.79	0.71

TABLE 4: Comparison of Experimental and Calculated a_H and a_F of the 1,2,3,4,5,6-Hexafluorocyclohexadienyl Radical, 4[•]

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(1)/\text{mT}$	$a_F(2,6)/\text{mT}$	$a_F(3,5)/\text{mT}$	$a_F(4)/\text{mT}$	$a_F(1)/\text{mT}$
exptl ²⁵		1.93	2.41	0.58	3.76	12.62
AM1//AM1		3.15				
B3LYP/6-31G*//AM1	0.799/0.751	4.73	2.34	-1.05	2.95	8.32
B3LYP/6-31G*//UHF/3-21G*	0.784/0.751	1.99	2.25	-0.82	3.02	12.56
BLYP/6-31G*//AM1	0.766/0.750	4.61	1.57	-0.49	2.05	8.89
BLYP/6-31G*//UHF/3-21G*	0.761/0.750	1.85	1.55	-0.35	2.12	12.94
INDO//UHF/3-21G*		3.29	10.99	7.10	11.60	27.70
B3LYP/6-31G*//B3LYP/6-31G*	0.785/0.751	1.82	2.17	-0.79	3.09	12.56
BLYP/6-31G*//BLYP/6-31G*	0.763/0.750	1.54	1.54	-0.36	2.16	12.49

TABLE 5: Comparison of Experimental and Calculated a_H of the 5-Hydro-2-methylfuran-4-yl Radical, 5[•]

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(4)/\text{mT}$	$a_H(3)/\text{mT}$	$a_H(5,5')/\text{mT}$	$a_H(2, \text{Me})/\text{mT}$
exptl ²⁶		1.370	0.186	3.493/3.530	1.294
AM1//AM1	0.937/0.756	-1.402	0.882	2.794	1.335
B3LYP/6-31G*//AM1	0.774/0.750	-1.564	0.364	3.541	1.553
B3LYP/6-31G*//UHF/STO-3G	0.775/0.750	-1.608	0.380	3.373	1.261
B3LYP/6-31G*//UHF/3-21G*	0.773/0.750	-1.612	0.352	3.317	1.313
BLYP/6-31G*//AM1	0.760/0.750	-1.329	0.144	3.670	1.475
BLYP/6-31G*//UHF/STO-3G	0.760/0.750	-1.369	0.160	3.520	1.200
BLYP/6-31G*//UHF/3-21G*	0.759/0.750	-1.372	0.146	3.447	1.255
INDO//UHF/3-21G*		-1.150	0.528	3.157	1.758
B3LYP/6-31G*//B3LYP/6-31G*	0.771/0.750	-1.570	0.302	3.659	1.335
BLYP/6-31G*//BLYP/6-31G*	0.759/0.750	-1.346	0.143	3.721	1.298

TABLE 6: Comparison of Experimental and Calculated a_H and a_P of the Hydrotrimethylphosphoranyl Radical, 6[•]

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	a_P/mT	a_H/mT	$a_H(3 \text{ Me})/\text{mT}$
exptl ²⁷		48.4	18.2	
AM1//AM1 ^b	0.756/0.750	^a	13.66	-0.3
B3LYP/6-31G*//AM1 ^b	0.751/0.750	7.97	3.89	1.2
B3LYP/6-31G*//UHF/3-21G* ^c	0.755/0.750	42.9	16.9	0.2
BLYP/6-31G*//AM1 ^b	0.751/0.750	7.09	3.32	1.1
BLYP/6-31G*//UHF/3-21G* ^b	0.753/0.750	34.7	3.77	-0.04
BLYP/6-31G*//UHF/3-21G* ^c	0.752/0.750	42.3	16.7	0.1
B3LYP/6-31G*//B3LYP/6-31G* ^c	0.755/0.750	44.0	17.5	0.1
BLYP/6-31G*//BLYP/6-31G* ^c	0.754/0.750	44.7	16.5	0.1

^a Not parametrized for P. ^b Methyl groups in a pyramidal arrangement; see formula 6b. ^c Trigonal bipyramidal geometry with the H atom in an axial position; see formula 6a.

AM1 method, the ³¹P coupling constant and the a_H for the single proton are about 1 order of magnitude too low. With the geometry calculated by the *ab initio* or the DFT procedures, however, the agreement between all experimental and theoretical hyperfine values is good (Table 6). Interestingly, the ³¹P coupling constant does not significantly alter depending on the type of functional used.^{21f,42} Moreover it must be noted that the geometry obtained from the AM1 calculations also exists as a minimum on the energy surface for the *ab initio* and the DFT techniques. Still, the trigonal-bipyramidal geometry (see also the formula) has a markedly lower energy than that presented in formula 6b. According to calculations, the bipyramidal geometry is strongly favored (B3LYP/6-31G*//B3LYP/6-31G*, 10.7 kcal·mol⁻¹; BLYP/6-31G*//BLYP/6-31G*, 9.3 kcal·mol⁻¹; and PMP2(full)/6-31G*//UHF/3-21G*, 13.1 kcal·mol⁻¹), affirming the structure suggested by Williams.²⁷

4.2. Radical Cations. The norbornadiene radical cation 7^{•+} has a_H values of -0.780 mT (4 H), 0.304 mT (2 H), and -0.049 mT (2 H).²⁸ The B3LYP/6-31G*//UHF/3-21G* calculated values almost exactly reproduce the experimental values. All the DFT procedures based on *ab initio* or AM1 geometries give a fair agreement in this case (Table 7). On the other hand, the a_H from the semiempirical methods AM1 and INDO deviate substantially from the experimental data. Former predictions of the a_H of the quadricyclane radical cation (8^{•+}) were -1.05 mT (4 H), 0.79 mT (2 H), and -0.4 mT (2 H), determined by *ab initio* methods.⁴³ These values only very roughly correspond to the hyperfine data of 0.51 mT (4 H), 0.66 mT (2 H), and 0.2 mT (2 H) established by time-resolved EPR.²⁹ Moreover this radical (8^{•+}) was also detected in a zeolite environment with a considerably different set of a_H : 0.98 mT (4 H), 0.72 mT (2 H), and 0.28 mT (2 H).⁴⁴ The procedures B3LYP/6-31G*//UHF/3-21G*, BLYP/6-31G*//UHF/3-21G* and B3LYP/6-31G*//

TABLE 7: Comparison of Experimental and Calculated a_H of the 2,5-Norbornadiene Radical Cation, 7^{+}

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(2,3,5,6)/\text{mT}$	$a_H(7, 2 \text{ H})/\text{mT}$	$a_H(1,4)/\text{mT}$
exptl ²⁸		-0.780	0.304	-0.049
AM1//AM1	0.754/0.7500	-0.523	0.054	0.008
B3LYP/6-31G*//AM1	0.753/0.750	-0.786	0.481	-0.052
B3LYP/6-31G*//UHF/STO-3G	0.769/0.750	-0.700	0.178	-0.145
B3LYP/6-31G*//UHF/3-21G*	0.753/0.750	-0.775	0.358	-0.049
BLYP/6-31G*//AM1	0.752/0.750	-0.747	0.579	-0.045
BLYP/6-31G*//UHF/STO-3G	0.758/0.750	-0.667	0.199	-0.109
BLYP/6-31G*//UHF/3-21G*	0.752/0.750	-0.736	0.435	-0.043
INDO//UHF/3-21G*		-0.476	-0.077	-0.020
B3LYP/6-31G*//B3LYP/6-31G*	0.752/0.750	-0.787	0.405	-0.050
BLYP/6-31G*//BLYP/6-31G*	0.752/0.750	-0.748	0.523	-0.042

TABLE 8: Comparison of Experimental and Calculated a_H of the Quadricyclane Radical Cation, 8^{+}

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(2,3,5,6)/\text{mT}$	$a_H(7, 2 \text{ H})/\text{mT}$	$a_H(1,4)/\text{mT}$
exptl ²⁹		0.51	0.20	0.66
AM1//AM1	0.754/0.750	-0.52	0.06	0.01
B3LYP/6-31G*//AM1	0.753/0.750	-0.79	-0.48	-0.05
B3LYP/6-31G*//UHF/STO-3G	0.754/0.750	-0.40	-0.22	0.73
B3LYP/6-31G*//UHF/3-21G*	0.754/0.750	-0.53	-0.22	0.61
BLYP/6-31G*//AM1	0.752/0.7500	-0.75	-0.59	-0.05
BLYP/6-31G*//UHF/STO-3G	0.752/0.750	-0.35	-0.19	0.71
BLYP/6-31G*//UHF/3-21G*	0.752/0.750	-0.48	-0.19	0.58
INDO//UHF/3-21G*		-0.45	-0.41	0.31
B3LYP/6-31G*//B3LYP/6-31G*	0.754/0.750	-0.49	-0.22	0.69
BLYP/6-31G*//BLYP/6-31G*	0.752/0.750	-0.46	-0.19	0.66

TABLE 9: Comparison of Experimental and Calculated a_H of the 1,8-Dimethylnaphthalene Radical Cation, 9^{+}

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(2,7)/\text{mT}$	$a_H(3,6)/\text{mT}$	$a_H(4,5)/\text{mT}$	$a_H(\beta,1,8, 2 \text{ CH}_3)/\text{mT}$
exptl ³⁰		0.245	0.116	0.573	0.825
AM1//AM1	0.872/0.761	-0.330	0.224	-0.813	0.764
B3LYP/6-31G*//AM1	0.762/0.750	-0.284	-0.051	-0.685	0.976
B3LYP/6-31G*//UHF/STO-3G	0.763/0.750	-0.245	-0.073	-0.667	0.795
B3LYP/6-31G*//UHF/3-21G*	0.762/0.750	-0.258	-0.064	-0.659	0.832
BLYP/6-31G*//AM1	0.754/0.750	-0.261	-0.091	-0.580	1.093
BLYP/6-31G*//UHF/STO-3G	0.754/0.750	-0.232	-0.104	-0.570	0.829
BLYP/6-31G*//UHF/3-21G*	0.754/0.750	-0.242	-0.097	-0.563	0.868
INDO//UHF/3-21G*		-0.206	-0.012	-0.552	0.987
B3LYP/6-31G*//B3LYP/6-31G*	0.762/0.750	-0.251	-0.086	-0.627	0.882
BLYP/6-31G*//BLYP/6-31G*	0.754/0.750	-0.243	-0.108	-0.546	0.913

TABLE 10: Comparison of Experimental and Calculated a_H of the Acenaphthene Radical Cation, 10^{+}

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(\beta,44)/\text{mT}$	$a_H(2,7)/\text{mT}$	$a_H(3,6)/\text{mT}$	$a_H(4,5)/\text{mT}$
exptl ³¹		1.318	0.313	0.059	0.659
AM1//AM1	0.877/0.762	1.142	-0.344	0.246	-0.845
B3LYP/6-31G*//AM1	0.763/0.750	1.450	-0.314	-0.023	-0.743
B3LYP/6-31G*//UHF/STO-3G	0.765/0.750	1.200	-0.214	-0.009	-0.755
B3LYP/6-31G*//UHF/3-21G*	0.763/0.750	1.242	-0.303	-0.025	-0.736
BLYP/6-31G*//AM1	0.754/0.750	1.595	-0.286	-0.066	-0.634
BLYP/6-31G*//UHF/STO-3G	0.755/0.750	1.336	-0.288	-0.056	-0.644
BLYP/6-31G*//UHF/3-21G*	0.754/0.750	1.378	-0.275	-0.067	-0.629
INDO//UHF/3-21G*		1.510	-0.219	-0.075	-0.539
B3LYP/6-31G*//B3LYP/6-31G*	0.760/0.750	1.357	-0.305	-0.037	-0.714
BLYP/6-31G*//BLYP/6-31G*	0.754/0.750	1.475	-0.280	-0.076	-0.611

/BLYP/6-31G, BLYP/6-31G*/BLYP/6-31G yield a_H values that correspond to those reported by Ishiguro et al.²⁹ (Table 8). The conspicuous difference of the a_H reported by Cromack et al.⁴⁴ may stem from matrix effects of the zeolite or a rearranged quadricyclane skeleton (which, however, does not correspond to 7^{+} , see above).

The Hückel MO model still is a method of choice to predict the a_H of radical ions of planar π radical ions because semiempirical calculations mostly yield poorer results (cf. Table 9). The use of *ab initio* methods with large basis sets is not feasible due to the size of the molecules consisting of extended π systems. To test whether the application of DFT is beneficial for delocalized π systems, we have selected 1,8-dimethylnaphthalene (**9**)³⁰ and acenaphthene (**10**),³¹ The results are presented in Tables 9 and 10. Whereas the a_H of the protons in the 2,7

and β positions are predicted adequately by AM1 and INDO, the a_H at the 3,6 positions deviate from experiment particularly with AM1 (Tables 9, 10). The DFT-calculated a_H values show a very good conformity with the experimental values.

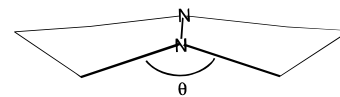
Radical cations derived from hydrazines or azo compounds have been of considerable interest.⁴⁵ The hyperfine coupling constant of ^{14}N nuclei, a_N , gives important insight into the spin distribution in these radicals, and it shows a distinctive dependence upon the pyramidalization at the N atom. There is much data available for these radical cations, and we have chosen the radical cations of tetramethylhydrazine (**11**),³² 1,2-di(*tert*-butyl)-1,2-dimethylhydrazine (**12**),³³ in which the a_N value decreases by 0.25 mT relative to **11**⁺, and 1,5-diazabicyclo[3.3.0]octane (**13**)³⁴ as well as **14**, where the hydrazine moiety is embedded in the bicyclic system.³³

TABLE 11: Comparison of Experimental and Calculated a_H and a_N of the Tetramethylhydrazine Radical Cation, $11^{+\bullet}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_N(2\text{ N})/\text{mT}$	$a_H(4\text{ CH}_3)/\text{mT}$
exptl ³³		1.34	1.27
AM1//AM1	0.757/0.7500	^a	1.03
B3LYP/6-31G**//AM1	0.754/0.750	1.26	1.41
B3LYP/6-31G**//UHF/STO-3G	0.754/0.750	1.20	1.23
B3LYP/6-31G**//UHF/3-21G*	0.754/0.750	1.17	1.27
BLYP/6-31G**//AM1	0.752/0.750	1.03	1.46
BLYP/6-31G**//UHF/STO-3G	0.752/0.750	0.94	1.29
BLYP/6-31G**//UHF/3-21G*	0.752/0.750	0.91	1.33
INDO//UHF/3-21G*		0.10	0.72
B3LYP/6-31G**//B3LYP/6-31G*	0.754/0.750	1.12	1.39
BLYP/6-31G**//BLYP/6-31G*	0.752/0.750	0.90	1.43

^a No conversion factor available.

The gradual decrease of the a_N (1.881, 1.76, 1.34, and 1.19 mT in $14^{+\bullet}$, $13^{+\bullet}$, $11^{+\bullet}$, and $12^{+\bullet}$, respectively; Tables 11–14) is only roughly paralleled in the calculated data. This is predominately due to the amount of pyramidalization at the N atoms established by the different geometry optimizations. For example in $13^{+\bullet}$ the pyramidalization angle θ between the two neighboring N–C bonds is (Figure 1) 153° , 167° , and 154° for AM1, UHF/3-21G*, and BLYP/6-31G*, respectively. The deviation from the minimum geometry affords only a small activation energy;³³ thus the ESR data for these N-centered radicals represent average values due to a fast motion ($>10^{-9}$ s) of the flexible NR_3 moiety. To illustrate this behavior, we have calculated the energies of differently pyramidalized NH_3

**Figure 1.** Interplanar angle in $13^{+\bullet}$ indicating the pyramidalization at the N atoms.

radical cations. According to DFT calculations (BLYP/6-31G*, B3LYP/6-31G*), the deviation from the minimum energy with a planar arrangement of the N atom can be up to 20° , while the energy increases by only *ca.* 1 kcal·mol^{−1}. This easily achievable bending leads to a_N that are *ca.* 0.2 mT higher than those of a planar $\text{NH}_3^{+\bullet}$.

4.3. Radical Anions. Most radical anions described in the literature are generated from planar π systems. A prototype of such ions is that of naphthalene (**15**). Here we describe the results for $15^{\bullet-}$ and study the influence of methyl substitution (β -protons), in the 1,8-dimethyl derivative $9^{\bullet-46}$ as well as the peri-strained acenaphthene $10^{\bullet-}$.⁴⁷

None of the semiempirical calculations yielded a reasonable agreement with the measured data. The a_H of the 2,3,6,7 positions of $15^{\bullet-}$ deviate by two orders of magnitude from experimental values. This type of disagreement is even more marked for $9^{\bullet-}$ and $10^{\bullet-}$, except for the β - a_H . However, the calculated results fit much better to the experimental data when the Fermi contact interaction is determined with DFT functionals (Tables 15–17). In the case of $9^{\bullet-}$, the assignment of the rather similar a_H of 0.169 and 0.178 mT to the 2,7 and 3,6 positions, respectively, was based on Hückel-type calculations,⁴⁶ and the predictions for these couplings were 0.146, and 0.209 mT (or

TABLE 12: Comparison of Experimental and Calculated a_H and a_N of the 1,2-Di(*tert*-butyl)-1,2-dimethylhydrazine Radical Cation, $12^{+\bullet}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_N(2\text{ N})/\text{mT}$	$a_H(2\text{ CH}_3)/\text{mT}$	$a_H(t\text{-Bu})/\text{mT}$
exptl ³³		1.19	1.19	not detected
AM1//AM1	0.757/0.750		1.08	−0.03
B3LYP/6-31G**//AM1	0.754/0.750	1.10	1.31	0.00
B3LYP/6-31G**//UHF/3-21G*	0.754/0.750	1.10	1.08	0.00
BLYP/6-31G**//AM1	0.752/0.750	0.86	1.36	0.01
BLYP/6-31G**//UHF/3-21G*	0.752/0.750	0.86	1.13	0.02
INDO//UHF/3-21G*		1.06	0.67	−0.05
B3LYP/6-31G**//B3LYP/6-31G*	0.754/0.750	1.05	1.19	0.01

TABLE 13: Comparison of Experimental and Calculated a_H and a_N of the 1,5-Diazabicyclo[3.3.0]octane Radical Cation, $13^{+\bullet}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_N(2\text{ N})/\text{mT}$	$a_H(\beta, 8\text{ H})/\text{mT}$	$a_H(\gamma, 4\text{ H})/\text{mT}$
exptl ³³		1.76	1.56	0.08
AM1//AM1	0.757/0.750		1.17	−0.03
B3LYP/6-31G**//AM1	0.754/0.750	1.89	1.50	−0.06
B3LYP/6-31G**//UHF/3-21G*	0.754/0.750	1.33	1.44	−0.07
BLYP/6-31G**//AM1	0.752/0.750	1.70	1.59	−0.05
BLYP/6-31G**//UHF/3-21G*	0.752/0.750	1.08	1.52	−0.06
INDO//UHF/3-21G*		1.13	0.89	−0.12
B3LYP/6-31G**//B3LYP/6-31G*	0.754/0.750	1.65	1.54	−0.06
BLYP/6-31G**//BLYP/6-31G*	0.752/0.750	1.54	1.57	−0.05

TABLE 14: Comparison of Experimental and Calculated a_H of the 2,3-Dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene Radical Cation, $14^{+\bullet}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_N(2\text{ N})/\text{mT}$	$a_H(\text{Me})/\text{mT}$	$a_H(1,4)/\text{mT}$	$a_H(5,6)/\text{mT}$	$a_H(7)/\text{mT}$	$a_H(8)/\text{mT}$
exptl ³³		1.881	1.277		0.374	0.214	0.139
AM1//AM1	0.757/0.750		1.072	−0.053	0.305	−0.126	−0.032
B3LYP/6-31G**//AM1	0.754/0.750	1.611	1.476	−0.014	0.365	−0.216	−0.133
B3LYP/6-31G**//UHF/STO-3G	0.754/0.750	1.668	1.181	−0.002	0.366	−0.223	−0.133
B3LYP/6-31G**//UHF/3-21G*	0.754/0.750	1.478	1.261	0.016	0.325	−0.232	−0.139
BLYP/6-31G**//AM1	0.752/0.750	1.400	1.531	−0.012	0.414	−0.195	−0.130
BLYP/6-31G**//UHF/STO-3G	0.752/0.750	1.458	1.230	0.000	0.419	−0.198	−0.126
BLYP/6-31G**//UHF/UHF/3-21G*	0.752/0.750	1.258	1.308	0.016	0.370	−0.207	−0.132
INDO//UHF/3-21G*		1.260	0.706	−0.057	0.353	−0.242	−0.059
B3LYP/6-31G**//B3LYP/6-31G*	0.754/0.750	1.818	1.303	−0.001	0.392	−0.210	−0.133
BLYP/6-31G**//BLYP/6-31G*	0.752/0.750	1.726	1.316	−0.013	0.443	−0.181	−0.119

TABLE 15: Comparison of Experimental and Calculated a_H of the Naphthalene Radical Anion, $15^{\bullet-}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(1,4,5,8)/\text{mT}$	$a_H(2,3,6,7)/\text{mT}$
exptl ³⁵		0.490	0.183
AM1//AM1	0.864/0.760	-0.707	-0.031
B3LYP/6-31G*//AM1	0.761/0.750	-0.660	-0.182
B3LYP/6-31G*//UHF/STO-3G	0.761/0.750	-0.656	-0.175
B3LYP/6-31G*//UHF/3-21G*	0.761/0.750	-0.651	-0.177
BLYP/6-31G*//AM1	0.754/0.750	-0.570	-0.186
BLYP/6-31G*//UHF/STO-3G	0.754/0.750	-0.567	-0.179
BLYP/6-31G*//UHF/3-21G*	0.754/0.750	-0.560	-0.181
INDO//UHF/3-21G*		-0.482	-0.052
B3LYP/6-31G*//B3LYP/6-31G*	0.761/0.750	-0.643	-0.185
BLYP/6-31G*//BLYP/6-31G*	0.754/0.750	-0.560	-0.188

TABLE 16: Comparison of Experimental and Calculated a_H of the 1,8-Dimethylnaphthalene Radical Anion, $9^{\bullet-}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(2,7)/\text{mT}$	$a_H(3,6)/\text{mT}$	$a_H(4,5)/\text{mT}$	$a_H(\beta, 2 \text{ CH}_3)/\text{mT}$
exptl ⁴⁶		0.169	0.178	0.460	0.460
AM1//AM1	0.866/0.760	-0.108	0.046	-0.743	0.583
B3LYP/6-31G*//AM1	0.760/0.750	-0.211	-0.143	-0.664	0.569
B3LYP/6-31G*//UHF/STO-3G	0.762/0.750	-0.219	-0.161	-0.615	0.454
B3LYP/6-31G*//UHF/3-21G*	0.761/0.750	-0.202	-0.141	-0.659	0.473
BLYP/6-31G*//AM1	0.754/0.750	-0.202	-0.162	-0.563	0.549
BLYP/6-31G*//UHF/STO-3G	0.754/0.750	-0.209	-0.170	-0.531	0.444
BLYP/6-31G*//UHF/3-21G*	0.754/0.750	-0.196	-0.158	-0.561	0.458
INDO//UHF/3-21G*		-0.118	-0.043	-0.501	0.741
B3LYP/6-31G*//B3LYP/6-31G*	0.761/0.750	-0.201	-0.159	-0.647	0.492
BLYP/6-31G*//BLYP/6-31G*	0.754/0.750	-0.202	-0.164	-0.563	0.479

TABLE 17: Comparison of Experimental and Calculated a_H of the Acenaphthene Radical Anion, $10^{\bullet-}$

calc of geom/spin (single point (Fermi)//geometry opt.)	$\langle s^2 \rangle$ before/after annihilation	$a_H(\beta, 4H)/\text{mT}$	$a_H(2,7)/\text{mT}$	$a_H(3,6)/\text{mT}$	$a_H(4,5)/\text{mT}$
exptl ⁴⁷		0.745	0.118	0.235	0.412
AM1//AM1	0.862/0.760	0.841	0.012	-0.067	-0.662
B3LYP/6-31G*//AM1	0.760/0.750	0.944	-0.128	-0.215	-0.602
B3LYP/6-31G*//UHF/STO-3G	0.762/0.750	0.803	-0.138	-0.229	-0.556
B3LYP/6-31G*//UHF/3-21G*	0.761/0.750	0.803	-0.117	-0.217	-0.595
BLYP/6-31G*//AM1	0.754/0.750	0.901	-0.137	-0.221	-0.515
BLYP/6-31G*//UHF/STO-3G	0.754/0.750	0.770	-0.145	-0.227	-0.482
BLYP/6-31G*//UHF/3-21G*	0.754/0.750	0.765	-0.128	-0.220	-0.509
INDO//UHF/3-21G*		0.967	-0.064	-0.047	-0.452
B3LYP/6-31G*//B3LYP/6-31G*	0.760/0.750	0.855	-0.112	-0.239	-0.579
BLYP/6-31G*//BLYP/6-31G*	0.754/0.750	0.808	-0.132	-0.228	-0.512

similar values depending on the perturbation parameters used to model the inductive and hyperconjugative effects of the methyl group substitution). The results presented in Table 15 reverse the former assignment. It must be added, however, that the solvent, the temperature, and the counterion can shift the experimental a_H by *ca.* 5%; such environmental effects are hitherto not accounted for by the theoretical models.

Hückel calculations for the a_H of $10^{\bullet-}$, representing a slightly strained alkylated naphthalene (which, as $9^{\bullet-}$, forms ion pairs with alkali-metal cations), give only poor agreement with the experimental data.⁴⁷ Table 17 indicates that the calculated and experimental data are in very good accord when the geometry is determined by *ab initio* 3-21G* or DFT and the Fermi contacts by the BLYP or B3LYP functionals.

4.4. General Comparison. The above examples have clearly indicated that the Fermi contact interaction is adequately described by the BLYP and B3LYP formalism. Within the scope of this work it is pertinent to test the Fermi contact interactions obtained from the semiempirical and DFT methods with those realized at the MP2 level. In Figure 2, the a_i of radicals $7^{\bullet+}$, $8^{\bullet+}$, $13^{\bullet+}$, and $15^{\bullet-}$ calculated with AM1, BLYP/6-31G*//UHF/3-21G*, and UMP2(full)/6-31G*//UHF/3-21G* are compared to the experimental data. For clarity the data points belonging to the same method are connected. It is evident that AM1 only roughly reproduces the experimental data, whereas the BLYP/6-31G*//UHF/3-21G* procedure closely resembles the measured a_i . This also holds for UMP2(full)/6-

31G*//UHF/3-21G* except for the naphthalene π radical anion $15^{\bullet-}$, where only the DFT methods give matching results (Table 15).

5. Conclusion

AM1 and INDO techniques only rarely lead to even fair agreement between the experimental and theoretical a_H values. A notable improvement is achieved if the Fermi contact interaction is calculated with a DFT method, with the use of the functionals BLYP and B3LYP.

When the geometry is determined by *ab initio* techniques (UHF/3-21G*) or DFT and the hyperfine coupling constants are derived from a DFT treatment, the agreement between the calculated and the experimental data reaches a considerable quality: the deviations decrease to *ca.* 10%. This conclusion is valid for all radicals treated in this study, *i.e.*, neutral radicals and radical ions with localized and delocalized spin and charge and different character (π to σ). As expected,⁴² for the results of the DFT calculations of a_i where i is not ^1H , some dependence on the functionals employed is observed; this is borne out in Tables 4–6 and 11–14.

In summary, we have shown that single-point DFT calculations of organic radicals and radical ions using the BLYP and B3LYP functionals give a_i values in good agreement with those established by ESR spectroscopy. Generally both functionals give satisfying proton hyperfine coupling constants. The

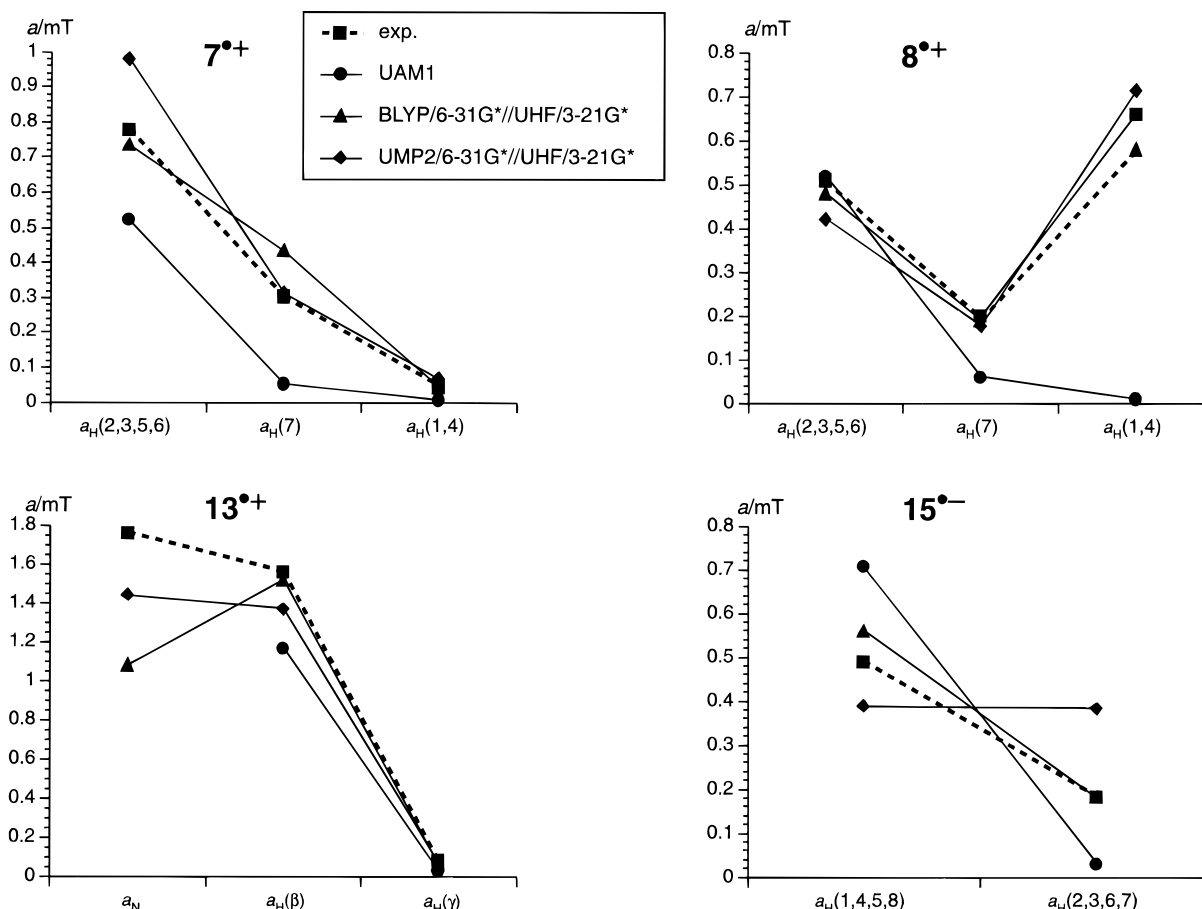


Figure 2. Comparison of the a_i of 7•+, 8•+, 13•+, and 15•- obtained from AM1, BLYP/6-31G*/UHF/3-21G*, and UMP2(full)/6-31G*/UHF/3-21G* with the experimental data.

predictions for the a_i of non-hydrogen nuclei, however, seem to be slightly better with the B3LYP functional. Preliminary tests indicate that DFT geometry optimizations and calculations of the Fermi contacts with the BPW91 functional (Becke's exchange^{40a} and Perdew and Wang's correlation⁴⁸ functional) also give promising results. Additional investigations on the influence of the AO basis sets are under way.⁴⁹

The prerequisite, a reliable geometry, can be typically taken from *ab initio* using UHF/3-21G*. Optimizations of the geometry with larger basis sets, if at all, only led to small improvements in the calculated Fermi contacts. Once again this had no relation to the significantly larger expenditure of computing resources.

It was the scope of this work to determine if there is an accurate and efficient procedure to obtain reliable a_i to improve the chance of a correct identification of an organic radical or radical ion. In this respect the above combination DFT/UHF/3-21G* fulfills this requirement. Geometry optimizations on the DFT level may proceed with shorter CPU times with the use of other programs such as DEMON or DGAUSS, thus leading to the preference of DFT geometry optimizations.

A further challenge will be the prediction of solvent and counterion effects on the hyperfine data of radical ions.

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