

Calculated Optimised Structure and Hyperfine Coupling Constant of Some Radical Adducts of 2-Methyl-2-Nitrosopropane

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Abstract

The ground state optimized structures of some radical adducts of 2-methyl-2-nitrosopropane in water, toluene and benzene solutions were calculated by using DFT (B3LYP) and HF methods with 6-311G(d, p) and LanL2DZ levels. As trapped radicals, H, OH, SO₃, CH₃, CCl₃ and C₆H₅ were used. The calculated isotropic hyperfine coupling constants of all the trapped radicals were seen to be in good agreement with the corresponding experimental data. From all the calculated data it was concluded that for hyperfine calculations the DFT method is superior relative to the HF method. Also the geometrical parameters for the ground state optimized structures of all the radical adducts were listed, the binding energies of all the trapped radicals and Anisotropic Spin Dipole Couplings in Principal Axis System were obtained.

Key Words: Electron paramagnetic resonance, DFT, HF, Radicals, Optimization

1. INTRODUCTION

Electron paramagnetic resonance (EPR) is a sophisticated spectroscopic technique that detects free radicals or inorganic complexes in chemical and biological systems. Unfortunately the lifetimes of most radicals generated with chemical reaction, irradiation or some other methods are short to be detected by EPR. So, the spin trapping method is used to increase of their lifetimes, and to detect them. There are two kinds of spin traps; nitrose and nitrone compounds. In nitrose compounds such as MNP(2-methyl-2-nitrosopropane) the radicals are trapped directly to the nitrose nitrogen while in nitrone compounds such as (PBN) a-phenyl-Ntert-butyl nitrone they are trapped to carbon adjacent to the nitrogen [1].

The isotropic hfcc's are very sensitive to the spin density at nucleus position, so, are very difficult to compute in a quantitative agreement with the experimental data [2]. The correlation of radical structure with spin adducts parameters was studied by Lawrence and et al. [3]. The hyperfine parameters of some radicals were studied by using the density function theory (DFT) and configuration-interaction (CI) methods [4]. Some authors have calculated the g-tensors of some organic radicals by Hartree-Fock (HF) method [5]. EPR parameters (g and a tensors) of sulfur centered radicals have been calculated using multiconfigurational self consistent field (MCSCF) response and DFT/ B3LYP methods [6].

Since only a few hfcc's of trapped radicals can be observed by EPR, the determination of structures of radical adducts is difficult. Therefore, theoretical calculations should be used for this.[7] The calculation of hfcc's of all nuclei in a radical structure, some being agreement with the experimental data, may contribute to interpret the properties of radical. [7] These calculations may also yield to further knowledge about the other properties (spin density, bond length, bond angle, binding energy of radical, i.e.) being difficult to observe, experimentally.[7]

So, in this study, the optimized structures and hyperfine coupling constants of some radical adducts of 2-methyl-2-nitrosopropane were calculated by using DFT B3LYP and HF methods with 6-311++G(d,p) and LanL2DZ levels. The calculated results were compared with the experimental data. The binding energies of all the trapped radicals were also determined. And anisotropic spin

dipole couplings in principal axis system of all the trapped radicals were calculated by using DFT B3LYP methods with 6-311G(d,p) level.

2. COMPUTATIONAL DETAILS

The structures of radical adducts of MNP were optimized by using spin-unrestricted DFT(B3LYP) and HF methods with 6-311++G(d, p) and LanL2DZ basis sets implemented in the polarizable continuum model (PCM) [8,9]. All calculations were performed using Gaussian 03 package [10] and Gauss-View molecular visualization programs [11] on the personal computer. These structures optimized. The binding energies of all the trapped radicals were calculated using supramolecular approach corrected for basis set superposition error (BSSE) according to Boys counterpoise method [12] at the optimized levels. Anisotropic spin dipole couplings in principal axis system of all the trapped radicals were calculated by using DFT(B3LYP) methods with 6-311G(d,p) level.

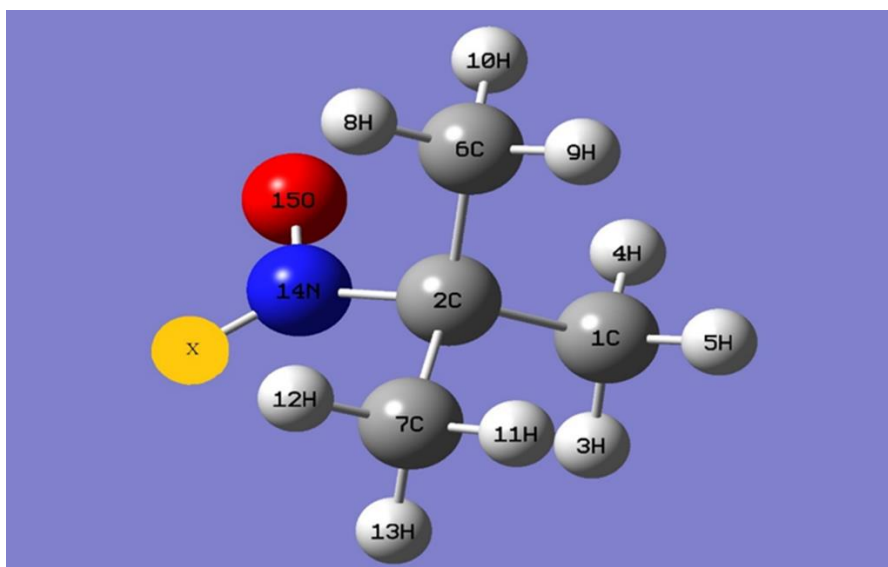


Fig. 1. Optimized structures of 2-methyl-2-nitrosopropane spin adducts (X; H, OH, SO₃, CH₃, CCl₃ C₆H₅).

3. RESULTS AND DISCUSSION

The calculated ground state optimized structures of the radical adducts of 2-methyl-2-nitrosopropane are shown in Fig. 1. The some selected geometrical parameters (bond length, bond angle and torsion angle) calculated at the B3LYP/6-311++G(d, p) level of theory are given in Table 1. As seen from the table there are slight differences between them and this causes some relative geometrical differences.

The hfcc's and energies for the ground state optimized structures of MNP-X radical products are tabulated in Tables 2. For comparison the experimental hfcc's are also given in the tables [1].

Taking into account that the calculated results, there is reasonable agreement between the calculated and experimental values. It can be concluded that for hyperfine calculations the DFT method is superior relative to the HF method. In Table 2 is also given the binding energies of all the trapped radicals by MNP calculated at the optimized levels.

In Table 3 anisotropic spin dipole couplings in principal axis system of all the trapped radicals were calculated by using DFT (B3LYP) methods with 6-311G(d,p) level. Anisotropic spin dipole couplings in principal axis system are two different presentations of the spin dipole term. Spin Dipole Couplings shows the eigen values of the spin dipole part of the effective spin Hamiltonian. Because this is a symmetric 3x3 tensor, only the 6 unique elements are shown. Diagonalizing the tensor gives the 3 principal values B_{aa}, B_{bb}, B_{cc} as the eigenvalues and the vectors from the origin for each principal value as the eigenvectors. These are the values interested in, most commonly reported in MHz by the computational/theoretical chemistry community and in Gauss by the spectroscopy community.

Table 1. Some selected geometrical parameters of 2-methyl-2-nitrosopropane radical product calculated at DFT(B3LYP) 6-311++G(d, p) level

	H	OH	SO ₃	CH ₃	CCl ₃	C ₆ H ₅
DIHEDRAL						
H(4)-C(1)-C(2)-N(14)	58.89688	61.92633	58.97275	58.05523	59.13371	56.90264
H(9)-C(6)-C(2)-N(14)	-178.71139	-178.21781	-176.56036	-178.03401	-171.79748	-176.59995
H(12)-C(7)-C(2)-N(14)	-59.86601	-64.72198	-64.26041	-65.70930	-57.28261	-58.68165
C(1)-C(2)-N(14)-O(15)	-58.01672	-48.71341	-53.91476	-48.93116	-54.30230	-55.05534
C(6)-C(2)-N(14)-O(15)	62.33489	70.95271	64.99563	70.49340	63.23279	63.75392
C(7)-C(2)-N(14)-O(15)	-177.84735	-167.74656	-173.24825	-168.51647	-174.31294	-175.88436
C(1)-C(2)-N(14)-X	127.61333	169.97124	149.87324	156.29958	139.19955	148.88844
C(6)-C(2)-N(14)-X	-112.03506	-70.36264	-91.21637	-84.27586	-103.26536	-92.30230
C(7)-C(2)-N(14)-X	7.78270	50.93809	30.53976	36.71428	19.18891	28.05942
ANGLES						
H(4)-C(1)-C(2)	110.58260	111.37517	111.16371	110.80301	111.28191	110.74692
H(13)-C(7)-C(2)	111.18946	110.97447	111.54451	111.34648	112.31108	112.08338
H(9)-C(6)-C(2)	110.01073	109.22089	109.53315	110.07076	108.99938	109.83425
C(7)-C(2)-C(1)	111.04953	110.68639	109.69500	109.85714	109.08027	110.15299
C(2)-N(14)-O(15)	121.99950	121.07589	117.45852	117.38889	114.91887	115.85950
C(1)-C(2)-N(14)	108.55566	106.35703	106.24563	107.58606	105.26337	107.18395
C(7)-C(2)-N(14)	106.83885	108.36116	111.24271	109.90307	114.89121	111.84305
C(2)-N(14)-X	120.61662	110.81052	122.81713	121.39366	126.56439	123.89402
O(15)-N(14)-X	117.15693	116.20394	115.62465	116.48609	117.21197	116.06824
BONDS						
H(4)-C(1)	1.09167	1.09029	1.09013	1.08942	1.08916	1.08971
H(13)-C(7)	1.09366	1.09284	1.09067	1.09334	1.08890	1.09160
H(9)-C(6)	1.09293	1.09286	1.09328	1.09314	1.09274	1.09307
C(6)-C(2)	1.53889	1.53687	1.53798	1.54059	1.53876	1.54053
C(7)-C(2)	1.53219	1.53185	1.53177	1.53472	1.53335	1.53180
C(1)-C(2)	1.53671	1.53175	1.53660	1.53470	1.53728	1.53462
N(14)-O(15)	1.28044	1.25563	1.26775	1.28228	1.27083	1.28434
C(2)-N(14)	1.48372	1.51507	1.52094	1.50351	1.54155	1.51693
N(14)-X	1.03289	1.42057	1.84493	1.46593	1.46455	1.43972

Table 2. Hpsc's and energies for the ground state optimized structures of MNP-X radical products in some solutions, and the bonding energies of the radicals									
Radicals-Solution		Hyperfine coupling constants (Gauss)					Energy (Hartree/particle)	Bonding energy of radical (Kcal/mol)	
		C(2)	H(3)	N(14)	O(15)	X			
Water	Exp.[1]			14.2	14.7				
MNP-H	DFT/ B3LYP	6311G++(d.p)	-6.06	-0.55	7.39	-11.01	$a_H = -15.72$	-288.457753	83.41
		LanL2DZ	-6.48	-0.65	14.10	-28.36	$a_H = -16.41$	-288.336208	71.78
	HF	6311G++(d.p)	-11.1	-0.75	19.83	-41.42	$a_H = -22.98$	-286.631472	99.83
		LanL2DZ	-11.6	-0.88	22.30	-63.55	$a_H = -24.03$	-286.482029	100.08
Water	Exp.[1]			4.4	28				
MNP-OH	DFT/ B3LYP	6311G++(d.p)	5.60	-0.11	25.35	-9.96	$a_O = -4.22$ $a_H = -2.08$	-363.667272	125.51
		LanL2DZ	3.42	-0.06	30.73	-23.78	$a_O = -6.01$ $a_H = -2.30$	-363.512971	124.20
	HF	6311G++(d.p)	-4.88	-0.49	36.62	-33.45	$a_O = -4.51$ $a_H = -0.84$	-361.469197	103.53
		LanL2DZ	-4.27	-0.20	28.70	-60.33	$a_O = 4.37$ $a_H = 4.76$	-361.278755	112.95
Water	Exp.[1]				14.8				
MNP-SO3	DFT/ B3LYP	6311G++(d.p)	-2.56	-0.34	12.36	-10.41	$a_S = -0.40$ $a_O = -0.37$ $a_O = 0.17$ $a_O = -1.45$	-911.918079	254.94
		LanL2DZ	1.34	-0.08	25.13	-25.51	$a_S = -0.00002$ $a_O = 0.40$ $a_O = -0.25$ $a_O = -1.17$	-523.452302	155.53
	HF	6311G++(d.p)	-8.43	-0.62	18.69	-41.74	$a_S = -4.49$ $a_O = -0.30$ $a_O = 0.93$ $a_O = -1.87$	-908.300735	222.33
		LanL2DZ	1.34	-0.08	25.13	-25.51	$a_S = -0.00002$ $a_O = 0.40$ $a_O = -0.25$ $a_O = -1.17$	-523.452302	155.48
Benzene	Exp.[1]			12.17	13.70				
MNP-CH3	DFT/ B3LYP	6311G++(d.p)	-3.05	-0.31	11.85	-10.47	$a_C = -3.51$ $a_H = 6.21$ $a_H = 22.14$ $a_H = 2.53$	-327.767435	125.56
		LanL2DZ	-4.12	-0.27	17.65	-27.68	$a_C = -4.98$ $a_H = 6.93$ $a_H = 20.92$ $a_H = 2.13$	-327.628796	124.82
	HF	6311G++(d.p)	-9.69	-0.63	21.71	-40.00	$a_C = -9.97$ $a_H = 5.92$ $a_H = 17.36$ $a_H = 2.30$	-325.659035	111.65
		LanL2DZ	-10.52	-0.63	24.27	-62.22	$a_C = -10.38$ $a_H = 6.55$ $a_H = 14.30$ $a_H = 1.93$	-325.486040	111.07

		Exp.[1]			12.56		$a_{CI}= 2.40$		
MNP-CCl3	DFT/ B3LYP	6311G++(d.p)	-3.61	-0.35	7.67	-10.35	$a_{C}=-7.16$ $a_{C}=4.16$ $a_{C}=5.32$ $a_{C}=-0.27$	-1706.597886	106.44
		LanL2DZ	-3.90	-0.34	10.763	-29.23	$a_{C}=-8.6$ $a_{C}=-0.00002$ $a_{C}=-0.00002$ $a_{C}=-0.00002$	-370.606724	52.95
	HF	6311G++(d.p)	-7.38	-0.57	15.64	-41.34	$a_{C}=-15.09$ $a_{C}=1.86$ $a_{C}=2.6$ $a_{C}=-0.71$	-1702.388197	104,96
		LanL2DZ	-6.50	-0.53	13.00	-64.53	$a_{C}=-16.38$ $a_{C}=-0.00008$ $a_{C}=-0.00009$ $a_{C}=-0.00005$	-367.778851	48.84
Benzene		Exp.[1]		1,80	12,3		$a_{H}=0,87$		
MNP-C6H5	DFT/ B3LYP	6311G++(d.p)	-3,17	-0,37	10,68	-10,15	$a_{H}=-1.13$ $a_{H}=-1.32$ $a_{H}=1.20$ $a_{H}=0.49$ $a_{H}=-0.95$ $a_{C}=-5.02$ $a_{C}=5.83$ $a_{C}=4.25$ $a_{C}=0.86$ $a_{C}=-0.89$ $a_{C}=1.25$	-519.548857	125.53
		LanL2DZ	-3.72	-0.30	16.41	-27.15	$a_{H}=-1.55$ $a_{H}=-1.67$ $a_{H}=0.7$ $a_{H}=1.27$ $a_{H}=-1.38$ $a_{C}=-6.63$ $a_{C}=6.42$ $a_{C}=5.23$ $a_{C}=-2.10$ $a_{C}=-2.35$ $a_{C}=3.25$	-519.335052	129.45
	HF	6311G++(d.p)	-8.83	-0.64	19.01	-40.93	$a_{H}=1.25$ $a_{H}=0.81$ $a_{H}=-1.90$ $a_{H}=-1.30$ $a_{H}=1.71$ $a_{C}=6.30$ $a_{C}=0.82$ $a_{C}=1.09$ $a_{C}=3.31$ $a_{C}=3.35$ $a_{C}=-3.28$	-516.207207	105.49
		LanL2DZ	-9.24	-0.66	20.42	-63.71	$a_{H}=0.25$ $a_{H}=0.01$ $a_{H}=-0.89$ $a_{H}=-0.49$ $a_{H}=0.85$ $a_{C}=-7.25$ $a_{C}=1.30$ $a_{C}=1.68$ $a_{C}=2.00$ $a_{C}=1.88$ $a_{C}=-2.03$	-515.943631	106.68

Table 3. Anisotropic Spin Dipole Couplings in Principal Axis System(gauss)

			H		OH	SO ₃	CH ₃	CCl ₃	C ₆ H ₅
1	C(13)	Baa	-1.698	-0.606	-0.352	-0.611	-0.575	-0.636	-0.606
		Bbb	-0.870	-0.310	-0.309	-0.338	-0.313	-0.263	-0.310
		Bcc	2.568	0.916	0.661	0.949	0.888	0.899	0.916
2	C(13)	Baa	-1.624	-0.579	-1.743	-0.724	-0.684	-0.450	-0.579
		Bbb	-1.401	-0.500	-1.508	-0.612	-0.577	-0.262	-0.500
		Bcc	3.024	1.079	3.251	1.336	1.261	0.713	1.079
3	H(1)	Baa	-3.387	-1.209	-1.151	-1.109	-1.060	-1.014	-1.030
		Bbb	-2.427	-0.866	-1.069	-1.023	-1.036	-0.961	-0.937
		Bcc	5.815	2.075	2.220	2.132	2.097	1.975	1.966
4	H(1)	Baa	-4.116	-1.469	-1.165	-1.399	-1.388	-1.478	-1.403
		Bbb	-2.144	-0.765	-0.997	-1.009	-1.044	-1.048	-0.993
		Bcc	6.260	2.234	2.162	2.408	2.432	2.526	2.396
5	H(1)	Baa	-2.170	-0.774	-0.586	-0.636	-0.617	-0.631	-0.611
		Bbb	-1.462	-0.522	-0.527	-0.558	-0.553	-0.519	-0.537
		Bcc	3.631	1.296	1.113	1.194	1.170	1.150	1.148
6	C(13)	Baa	-3.003	-1.072	-1.234	-1.113	-1.143	-0.886	-1.062
		Bbb	-2.260	-0.806	-1.021	-0.811	-0.867	-0.492	-0.708
		Bcc	5.263	1.878	2.256	1.924	2.010	1.378	1.770
7	C(13)	Baa	-0.924	-0.330	-0.344	-0.258	-0.300	-0.199	-0.243
		Bbb	-0.492	-0.176	-0.316	-0.237	-0.262	-0.187	-0.207
		Bcc	1.416	0.505	0.660	0.495	0.562	0.386	0.450
8	H(1)	Baa	-3.513	-1.254	-1.208	-1.141	-1.132	-0.971	-1.071
		Bbb	-2.225	-0.794	-0.494	-0.704	-0.623	-0.681	-0.689
		Bcc	5.738	2.047	1.702	1.845	1.755	1.652	1.760
9	H(1)	Baa	-2.388	-0.852	-0.989	-0.878	-0.899	-0.740	-0.851
		Bbb	-1.395	-0.498	-0.365	-0.452	-0.439	-0.477	-0.438
		Bcc	3.783	1.350	1.354	1.330	1.338	1.217	1.289
10	H(1)	Baa	-4.340	-1.549	-1.528	-1.651	-1.596	-1.681	-1.665
		Bbb	-1.815	-0.648	-0.394	-0.623	-0.553	-0.870	-0.680
		Bcc	6.155	2.196	1.922	2.274	2.149	2.551	2.345
11	H(1)	Baa	-1.523	-0.543	-0.588	-0.516	-0.521	-0.438	-0.486
		Bbb	-1.318	-0.470	-0.491	-0.444	-0.454	-0.403	-0.415
		Bcc	2.840	1.014	1.079	0.960	0.974	0.841	0.900
12	H(1)	Baa	-2.640	-0.942	-0.903	-0.778	-0.776	-0.671	-0.783
		Bbb	-2.526	-0.901	-0.858	-0.745	-0.740	-0.645	-0.669

		Bcc	5.166	1.843	1.761	1.523	1.516	1.316	1.452
13	H(1)	Baa	-2.764	-0.986	-1.151	-0.921	-0.992	-0.693	-0.811
		Bbb	-2.524	-0.900	-1.026	-0.876	-0.906	-0.645	-0.744
		Bcc	5.287	1.887	2.177	1.797	1.898	1.338	1.555
14	N(14)	Baa	-27.095	-9.668	-9.866	-9.106	-9.230	-8.119	-8.687
		Bbb	-26.581	-9.485	-9.616	-8.923	-9.011	-7.725	-8.419
		Bcc	53.676	19.153	19.482	18.029	18.242	15.844	17.106
15	O(17)	Baa	83.161	29.674	24.291	29.336	29.493	32.109	29.610
		Bbb	78.564	28.034	23.085	27.676	28.002	30.608	28.096
		Bcc	-161.725	-57.707	-47.376	-57.013	-57.495	-62.717	-57.707

4. CONCLUSIONS

The optimized ground state structures of some radical adducts of 2-methyl-2-nitrosopropane in some solutions were determined by using DFT(B3LYP) and HF methods with 6-311++G(d, p) and LanL2DZ levels. Selected radicals are H, OH, SO₃, CH₃, CCl₃ and C₆H₅ respectively. The calculated isotropic hyperfine coupling constants were seen to be in agreement with the experimental results. From all the calculated data it was seen that in hyperfine calculations the DFT method is better than the HF method. Also the calculated geometrical parameters (bond length, bond angle and torsion angle) and anisotropic spin dipole couplings in principal axis System for all the radical products were listed, and the binding energies of all the trapped radicals were determined.

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