



Calculated Hyperfine Coupling Constants And Geometric Parameters For 3,3,5,5-Tetramethylpyrroline-N-Oxide Radical Products With EPR Spin Trapping

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Abstract: The optimised structures of some radical adducts of 3,3,5,5-tetramethylpyrroline-N-oxide were computed by using DFT and HF methods with 6-311G(d, p) and LanL2DZ levels. As trapped radicals H,OH,OOH,O₂,CO₂,N₃,SO₄ were used.

The calculated isotropic hyperfine coupling constants of all the trapped radicals have seen to be in a great deal agreement with the corresponding experimental data. It was finalized that for hyperfine calculations the DFT method is superior relative to the HF method. In addition to the geometrical parameters for the ground state optimized structures of all the radical adducts were enriched, the binding energies of all the trapped radicals.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy is known as the “gold standard” for the detection and characterisation of radicals in chemical, biological and medical systems.[1] 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. Spin trapping is generally used in electron paramagnetic resonance spectroscopy to identify short lived free radicals. There are two kinds of spin traps; nitroso and nitron compounds. In nitroso compounds such as MNP(2-methyl-2-nitrosopropane) the radicals are trapped directly to the nitroso nitrogen while in nitron compounds such as (PBN) α -phenyl-N-tert-butyl nitron they are trapped to carbon adjacent to the nitrogen [2]. Nitroso spin traps have an advantage in that the initial radical becomes attached directly to the nitroso nitrogen atom, and is therefore in close

proximity to the unpaired electron localized on the nitroxide function. This usually results in the detection of additional distinctive hyperfine couplings from magnetic nuclei present in the added radical. The size and nature of these couplings can provide critical data with regard to the identify of the added radical. A number of compilations of radical adduct data are available. [1] Nitroso traps have a disadvantage in that they form long-lived adducts with a more limited number of radicals (mostly carbon-centred species and alkoxy radicals) than nitron traps [3,4,5]. Most nitroso traps are also thermally and photochemically unstable resulting in increased background/higher artifactual signals.

Nitrones, including DMPO (5, 5-dimethyl 1-pyrroline N-oxide, DEPMPO (5-diethoxyphosphoryl-5-methyl-1-pyrroline N-oxide, PBN (N-tert-butyl- α -phenylnitron) typically yield a wider spectrum of long-lived adducts [5]

The identity of free radicals has been revealed with the g-values and nuclei hyperfine coupling constants. The hyperfine coupling constant due to

β proton of nitroxide radical can be determined $a_{\beta}=B_0+B_1\cos^2$ [17]. B_0 is spin polarization contribution, θ is the angle between the P_{π} orbital of the nitrogen and projection of CH bond to the P_{π} orbital plane. The isotropic hyperfine coupling constants are very sensitive to the spin density at nucleus position, that's why, are very difficult to compute in a quantitative agreement with the experimental data [6]. The correlation of radical structure with spin adducts parameters had studied by Lawrence and et al. [7]. The hyperfine parameters of some radicals were studied by using the density function theory (DFT) and configuration-interaction (CI) methods [8]. Some authors have calculated the g-tensors of some organic radicals by Hartree Fock (HF) method [9]. EPR parameters (g and a tensors) of sulfur centered radicals have been calculated using multiconfigurational self consistent field (MCSCF) response and DFT/ B3LYP methods [10].

Since only a few hyperfine coupling constants of trapped radicals can be observed by electron paramagnetic resonance, the determination of structures of radical adducts is difficult. So, theoretical calculations should be used for this.[11] The calculation of hyperfine coupling constants of all nuclei in a radical structure, some being agreement with the experimental data, may contribute to interpret the properties of radical. [11] 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 hard to observe, experimentally.[11] In our previous study the hyperfine coupling constants on the ground state optimised structures of some PBN radical adducts in water and benzene solutions have been calculated by DFT and HF methods[11]So, in this study, the optimized structures and hyperfine

coupling constants of some radical adducts of 3,3,5,5-tetramethylpyrroline-N-oxide were calculated by using DFT B3LYP and HF methods with 6-311++G(d,p) and LanL2DZ basic sets. The calculation results were compared to the experimental data. The binding energies and geometric parameters of all the trapped radicals were also determined.

II. COMPUTATIONAL DETAILS

The 3,3,5,5-tetramethylpyrroline-N-oxide radical adducts were optimised in water and benzene solutions 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) [12,13]. All calculations were performed using Gaussian 03 package [14] and Gauss-View molecular visualization programs [15] 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 [16] at the optimized levels.

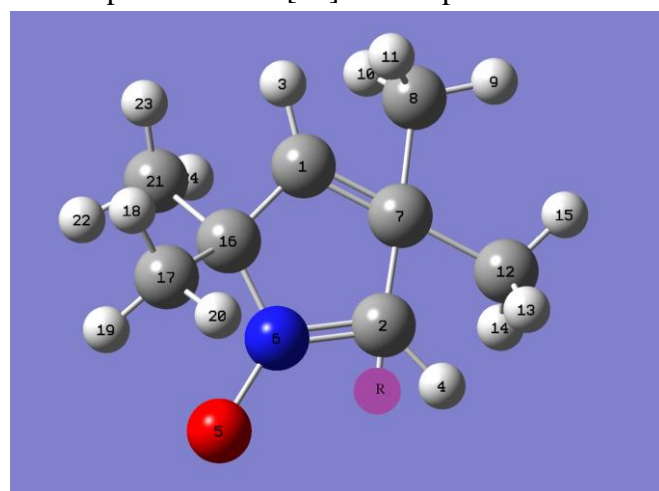


Fig.1. Optimised structures of all the radical products of 3,3,5,5-tetramethylpyrroline-N-oxide



III. RESULT AND DISCUSSION

The ground state optimized structures of the radical adducts of 3,3,5,5-tetramethylpyrroline-N-oxide are shown in Fig. 1. The some geometrical parameters such as bond length, bond angle and torsion angle were 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. From the table it can be understand some geometric details about effect of the trapped radicals on the structure 3,3,5,5-tetramethylpyrroline-N-oxide and about connection positions of the radicals.

The hyperfine coupling constants and energies for the ground state optimized structures of 3,3,5,5-tetramethylpyrroline-N-oxide-R radical products are listed in Tables 2. For comparison the experimental hyperfine coupling constants are also given in the tables 2. Taking into account that the calculated results, there is reasonable agreement between the calculated and experimental values. From the obtained correlation coefficients R^2 , it is also found that the DFT B3LYP/LANL2DZ level is generally more suitable than the other levels with a 0.82 value of R^2 . It can be concluded that for hyperfine calculations the DFT method is superior relative to the HF method.

In Tables 2 are also given the binding energies of all the trapped radicals by 3,3,5,5-tetramethylpyrroline-N-oxide calculated at the optimized levels.

IV. CONCLUSIONS

The optimized ground state structures of some radical adducts of 3,3,5,5-tetramethylpyrroline-N-oxide in water and benzene solutions were determined by using DFT(B3LYP) and HF

methods with 6-311++G(d, p) and LanL2DZ levels. Selected radicals are H, OH, OOH, O₂, CO₂, N₃ and SO₄ 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. The calculated geometrical parameters such as bond length, bond angle and torsion angle for all the radical products have been listed, and the binding energies of all the trapped radicals were obtained. The most tight binding radical was found H and the most lost binding radical was found N₃.

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Table 1. Some selected geometrical parameters of 3,3,5,5-tetramethylpyrroline-N-oxide radical product calculated at DFT(B3LYP) 6-311++G(d, p) level

Parameter	H	OH	OOH	O ₂	CO ₂	N ₃	SO ₄
DIHEDRAL							
C(16)-N(6)-C(2)-H(4)	-179.99	-180.56	-180.14	-180.75	-181.65	-180.99	-181.21
O(5)-N(6)-C(2)-H(4)	175.03	176.54	177.65	175.65	175.08	175.06	176.44
C(12)-C(7)-C(2)-H(4)	42.99	42.15	42.88	43.03	42.65	43.69	42.85
C(7)-C(2)-N(6)-O(5)	-179.99	-179.45	-179.36	-179.56	-179.25	-179.65	-179.55
C(1)-C(16)-N(6)-O(5)	179.99	179.26	179.47	179.32	179.85	179.54	179.63
C(16)-N(6)-C(2)-R	-173.28	-173.21	-172.66	-173.56	-173.58	-173.96	-172.24
C(12)-C(7)-C(2)-R	-55.25	-63.58	-78.21	-85.21	-82.56	-72.24	-73.21
O(5)-N(6)-C(2)-R	6,71	7.54	12.54	15.54	14.45	11.22	7.65
ANGLES							
C(16)-N(6)-O(5)	121.47	120.32	121.63	120.54	121.65	122.24	120.52
C(2)-N(6)-O(5)	130.11	132.21	132.32	130.63	130.52	130.52	131.94
N(6)-C(2)-H(4)	126.44	126.21	126.65	126.32	126.44	126.45	126.24
N(6)-C(16)-C(17)	86.11	86.21	85.54	85.26	86.546	87.32	86.24
C(7)-C(2)-H(4)	126.37	124.51	125.01	124.55	124.65	124.32	125.29
C(16)-C(1)-C(7)	108.417	108.24	108.22	107.21	107.51	108.21	108.91
C(2)-C(7)-C(1)	107.18	107.21	106.94	106.99	107.02	107.32	106.27
C(1)-C(16)-C(21)	86.11	86.214	86.524	86.251	87.20	86.55	86.21
N(6)-C(2)-R	77.39	78.54	85.12	86.54	100.54	87.99	87.54
C(7)-C(2)-R	172.06	180.64	178.54	179.65	177.78	178.65	175.03
BONDS							
N(6)-O(5)	1.43	1.42	1.45	1.41	1.42	1.43	1.42
C(16)-N(6)	1.39	1.37	1.36	1.37	1.38	1.38	1.37
C(2)-N(6)	1.40	1.41	1.42	1.41	1.40	1.41	1.42
C(2)-H(4)	0.96	0.98	0.96	0.97	0.97	0.96	0.96
C(7)-C(2)	1.43	1.42	1.41	1.42	1.42	4.41	1.43
C(16)-C(17)	1.54	1.51	2.49	1.51	1.52	1.50	1.51
C(16)-C(21)	1.52	1.49	1.51	1.52	1.52	1.51	1.51
C(1)-C(7)	1.40	1.42	1.40	1.42	1.41	1.43	1.40
C(7)-C(2)	1.43	1.41	1.42	1.42	1.41	1.41	1.42
C(7)-C(8)	1.54	1.54	1.54	1.53	1.53	1.51	1.53
C(7)-C(12)	1.51	1.53	1.51	1.51	1.52	1.52	1.51
C(2)-R	0.84	1.21	3.52	2.85	3.56	2.96	3.58



Table 2. Hyperfine coupling constants and energies for the ground state optimized structures of 3,3,5,5-tetramethylpyrroline-N-oxide -R radical products in water and benzene solutions, and the bonding energies of the radicals

3,3,5,5-tetramethylpyrroline-N-oxide -R Methods		Hyperfine coupling constants (Gauss)					Energy (Hartree/particle)	Bonding energy of radical (Kcal/mol)
		C	H _β	N	O	R		
BENZENE	Exp.[1]		18.29	14.61				
	6311G++(d.p)	-8.66	17.95	14.02	-	$a_H=12.5$	-384.235652	93.54
	DFT/B3LYP LanL2DZ	-8.35	19.56	20.5	-	$a_H=13.61$	-384.554221	98.54
					10.95			
H	6311G++(d.p)	-6.54	20.21	24.54	-	$a_H=15.62$	-382.215454	101.59
	HF LanL2DZ	-6.51	20.54	23.94	-	$a_H=15.21$	-382.524121	102.54
					14.21			
					14.32			
WATER	Exp.[1]		16.88	15.30				
	6311G++(d.p)	-6.51	16.54	14.64	-	$a_O=-4.23$	-615.24121	65.41
	DFT/B3LYP LanL2DZ	-6.84	16.98	14.89	-	$a_H=-0.79$	-615.23454	61.52
					11.64	$a_O=-4.65$		
OH	6311G++(d.p)	-5.32	18.21	20.51	-	$a_H=-0.81$	-610.54541	74.54
	HF LanL2DZ	-5.12	17.95	21.50	-	$a_O=-2.51$	-610.21216	76.85
					14.10	$a_H=-0.45$		
					14.62	$a_O=-2.10$		
						$a_H=-0.39$		
WATER	Exp.[1]		20.0	15.7				
	6311G++(d.p)	-9.21	20.86	15.01	-	$a_O=-3.45$	-567.295411	81.75
	DFT/B3LYP LanL2DZ	-9.32	21.54	15.95	-	$a_O=-3.12$	-567.321545	87.54
					12.65	$a_H=-0.85$		
OOH	6311G++(d.p)	-9.23	23.54	18.31	-	$a_O=-3.65$	-558.224545	83.45
	HF LanL2DZ	-9.45	23.98	18.32	-	$a_O=-3.40$	-558.321212	89.75
					15.12	$a_H=-0.78$		
					15.65	$a_O=-2.45$		
						$a_H=-2.21$		
						$a_O=-0.62$		
						$a_O=-2.52$		
						$a_H=-2.31$		
						$a_O=0.05$		
BENZENE	Exp.[1]		7.95	13.38				
	6311G++(d.p)	-	6.45	14.02	-	$a_O=-4.62$	-761.541265	75.52
	DFT/B3LYP LanL2DZ	-	6.99	14.11	-	$a_O=-2.45$	-761.545421	78.41
		12.45			11.02			
O2	6311G++(d.p)	-	8.12	15.98	-	$a_O=-3.87$	-722.545412	74.58
	HF LanL2DZ	-	8.14	16.01	-	$a_O=-2.75$	-722.215453	76.58
		13.30			16.60			
					16.82			
		13.25				$a_O=-0.09$		



Table 2. Contd.

3,3,5,5-tetramethylpyrroline-N-oxide –R		Hyperfine coupling constants (Gauss)					Energy	Bonding
Methods		C	H _β	N	O	R	(Hartree/particle)	energy of radical (Kcal/mol)
BENZENE	Exp.[1]		19.85	15.71				
	6311G++(d.p)	-8.45	20.06	16.50	-11.03	$a_C=-7.41$	-795.3124151	90.56
	DFT/ B3LYP					$a_O=-4.12$ $a_O=-2.02$		
CO2	LanL2DZ	-8.70	20.11	16.71	-11.41	$a_C=-7.85$	-795.2121211	89.54
						$a_O=-3.12$ $a_O=-2.41$		
	6311G++(d.p)	-8.23	24.45	18.21	-13.55	$a_C=-8.05$	-780.2121212	91.68
HF						$a_O=-5.47$ $a_O=-3.77$		
	LanL2DZ	-8.21	24.77	18.45	-13.41	$a_C=-8.96$	-780.1221212	91.23
						$a_O=-5.12$ $a_O=-3.19$		
WATER	Exp.[1]		14.88	14.88		2.98		
	6311G++(d.p)	-4.88	13.01	12.45	-10.65	$a_N=2.09$	-531.2565896	58.12
	DFT/ B3LYP					$a_N=2.23$ $a_N=2.96$		
N3	LanL2DZ	-4.21	13.52	12.88	-10.98	$a_N=1.96$	-531.24832223	57.51
						$a_N=2.11$ $a_N=3.09$		
	6311G++(d.p)	-6.23	10.88	10.23	-20.22	$a_N=1.65$	-528.2464321	53.54
HF						$a_N=2.05$ $a_N=2.85$		
	LanL2DZ	-6.25	10.23	10.12	-20.34	$a_N=1.21$	-528.212125	53.64
						$a_N=2.02$ $a_N=2.98$		



Table 2. Contd.

3,3,5,5-tetramethylpyrroline-N-oxide –R		Hyperfine coupling constants (Gauss)					Energy	Bonding	
Methods		C	H _β	N	O	R	(Hartree/particle)	energy of radical (Kcal/mol)	
WATER	Exp.[1]		8.34	14.04					
	6311G++(d.p)	-8.64	8.95	14.85	-12.24	$a_S=14.65$	-827.5212111	63.25	
	DFT/ B3LYP						$a_O=-2.54$		
							$a_O=2.63$		
							$a_O=-2.58$		
							$a_O=4.56$		
	LanL2DZ	-8.71	8.32	14.90	-12.87	$a_S=15.02$	-827.21212121	64.21	
						$a_O=-2.78$			
						$a_O=-2.84$			
	SO4						$a_O=2.54$		
						$a_O=6.22$			
6311G++(d.p)		-9.52	9.21	18.24	-14.65	$a_S=18.54$	-821.2454556	67.24	
HF							$a_O=-6.54$		
							$a_O=-7.12$		
							$a_O=3.45$		
						$a_O=10.57$			
LanL2DZ	-9.24	9.69	19.05	-14.12	$a_S=18.78$	-821.6554764	67.68		
					$a_O=-6.12$				
					$a_O=-7.12$				
					$a_O=4.12$				
					$a_O=10.85$				