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PHYSICAL CHEMISTRY OF SOLUTIONS

Calculated Hyperfine Coupling Constants for 5,5-Dimethyl-1-pyrroline N-Oxide Radical Products in Water and Benzene[1]

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Abstract—The optimized structures of some radical adducts of 5,5-dimethyl-1-pyrroline N-oxide were computed by different methods on ESR spectra. As trapped radicals, H, N_3, NH_2, CH_3, CCl_3, OOH in water and F, OH, CF_3, CH_2OH, OC_2H_5 in benzene solutions were used. The calculated isotropic hyperfine coupling constants of all the trapped radicals were compared with the corresponding experimental data. The hyperfine coupling constant due to the β proton of the nitroxide radical was seen to be consist with the McConnel's relation $\alpha_\beta = B_0 + B_1\cos^2\theta$ and, to be effected with the opposite spin density of oxygen nucleus bonded to the nitrogen. It was concluded that in hyperfine calculations the DFT(B3PW91)/LanL2DZ level is superior computational quantum model relative to the used other level. Also, the study has been enriched by the computational of the optimized geometrical parameters, the hyper conjugative interaction energies, the atomic charges and spin densities for all the radical adducts.

Keywords: hyperfine constant, DMPO, ESR, DFT, binding energy

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INTRODUCTION

Spin-trapping is usually used in electron spin resonance (ESR) spectroscopy to identify short-lived free radicals. There are two kinds of spin traps; nitrose and nitrone compounds. In nitrose compounds such as MNP (2-methyl-2-nitrosopropone) the radicals are trapped directly to the nitrose nitrogen while in nitrone compounds such as 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and N-tert-butyl-α-phenylnitrone (PBN) they are trapped to carbon adjacent to the nitrogen. The identification of the free radicals has been revealed with the *g*-values and the nuclei's hyperfine coupling constants. The characteristic feature of trapped radical by MNP, PBN, or DMPO is the triplet and doublet hyperfine splittings due to the N nucleus ($I = 1$) and β hydrogen nucleus ($I = 1/2$), respectively. The hyperfine coupling constant (hfcc) due to the β proton of the nitroxide radical can be given by the McConnell's relation $\alpha_\beta = B_0 + B_1\cos^2\theta$ [1]. Where B_0 is the spin polarization contribution (0–3.5), B_1 represents the hyper conjugative contribution (~50), and θ is the angle between the P_π orbital of the nitrogen and the projection of the CH bond to the P_π orbital plane.

A wide range of DMPO adducts with alkoxyl radicals have been synthesized, and the hfcc's have been determined in different experimental conditions [2]. Hfcc's for some spin adducts with popular spin traps have extensively been tabulated by Buettner [3]. Since the hfcc's of only a few nuclei in a trapped radical can be observed by ESR, the determination of structural properties of radical adduct is difficult. So, the computing of optimized structure, entire nuclei's hfcc's, spin densities, atomic charges and i.e., of a spin adduct may contribute to interpret its properties by theoretical approaches. Unfortunately, since the isotropic hfcc's are very sensitive to spin density at nucleus position it is very difficult to compute in a quantitative agreement with experimental data [4]. The hfcc's of the N and F nuclei on some radical adducts of 4-hydroxy-5,5-dimethyl-2-trifluoromethylpyrroline-1-oxide (FDMPO) have been computed at the DFT(B3LYP)/6-31G(*d,p*) and /6-31G++(*d,p*) levels and, compared to experimental data [5]. The effect of taxifolin on the production of hydroxyl and C-centered radicals has been investigated using ESR spin trapping, and the hfcc's of the N and F nuclei have been calculated for FDMPO/taxifolin spin adduct by using the DFT(B3LYP) method and, seen to be provided a reasonable agreement with the experimental data [6].

[1] The article is published in the original.

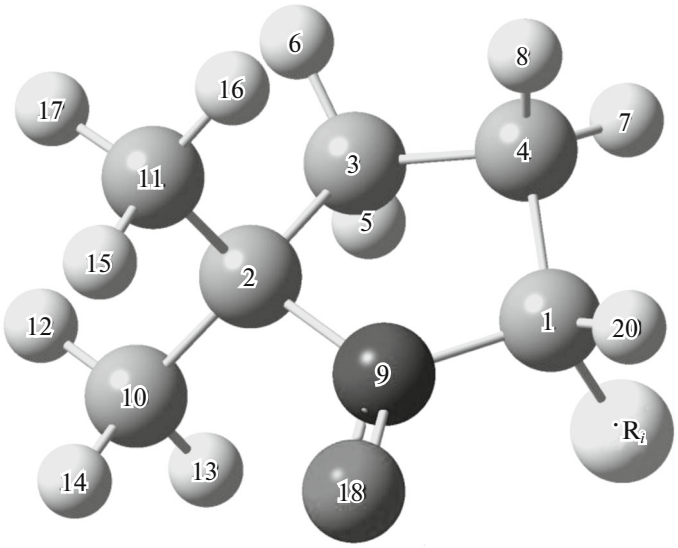

Fig. 1. Optimized structures of all the radical products of DMPO.

In our previous study the hfcc's on the ground state optimized structures of some PBN radical adducts in water and benzene solutions have been calculated by the DFT and HF methods [7]. In this study, the hfcc's on the optimized structures of some DMPO radical adducts have been calculated by using the DFT (B3LYP, B3PW91, and PBEPBE) and HF methods with 6-311++G(*d*,*p*) and LanL2DZ basic sets. The calculated results have been compared with the corresponding experimental data. In addition the radical's binding energies, hyper conjugative energies, atomic spin densities and atomic charges for all the radical products have been obtained to yield a further knowledge which contributes to interpret the structural properties of the radicals.

COMPUTATIONAL METHODS

The DMPO radical adducts have been optimized in water and benzene solutions by using the doublet spin-ground state unrestricted/DFT (B3LYP, B3PW91, and PBEPBE) and HF methods with 6-311++G(*d*,*p*) and LanL2DZ basic sets. The computations have been realized by the matrix inversion solution method in the polarizable continuum model (PCM) [8, 9]. All the calculations have been performed using Gaussian 09 package [10] and Gauss–View molecular visualization programs [11] on the personal computer. The binding energies of all the trapped radicals have been calculated using supramolecular approach corrected for basis set superposition error (BSSE) according to Boys counterpoise method [12]. Natural bond orbital (NBO) analysis [13–15] have been performed to evaluate natural population analysis (NPA) charges and hyper conjugative interaction energies at DFT (B3LYP) with 6-311++G(*d*,*p*) level.

RESULTS AND DISCUSSION

The ground state optimized structures of all the DMPO/$^{\bullet}R_i$ radical products ($^{\bullet}R_i$ = H, N_3, NH_2, CH_3, CCl_3, OOH in water and $^{\bullet}R_i$ = F, OH, CF_3, CH_2OH, OC_2H_5 in benzene solutions) are shown in Fig. 1. The selected geometrical parameters (bond length, bond angle and torsion angle) according with the atom numberings in the figure have been tabulated in Table 1. From the table it can be understand some geometric details about the effects of the trapped radicals on the structure of DMPO and, about the connection positions of the radicals. It also provides us the comparison chance between the selected parameters in water and benzene solutions. As an example the O18–N9–C2 angle is the highest for all the DMPO/$^{\bullet}$R radical products. This can be attributed that the formed intra-molecular interaction between the O18 atom and the trapped radicals, $^{\bullet}R_i$'s. The isotropic hfcc's of some nuclei computed on the ground state optimized structures of all the DMPO/$^{\bullet}R_i$ products in water and benzene solutions are given in Tables 2 and 3, respectively. For comparison the experimental hfcc's [3] are also given in the table. As seen there are reasonable agreements between the experimental and computed hfcc's. From the obtained correlation coefficients (R^2), it is also found that the DFT(B3PW91)/LanL2DZ level is generally more suitable than the other levels with a 0.86 value of R^2. In Tables 2 and 3 are also given the binding energies of all the trapped radicals. So, we can say that the most tight-binding radical is $^{\bullet}$H while the most lost-binding radical is $^{\bullet}$OOH. From these tables we can also see that the sign of the hfcc's of the N9 and O18 nuclei is opposite since the ferromagnetic interactions between the neighbor atoms can align electron spins parallel pro-

Table 1. Some selected geometrical parameters of all the radical products of DMPO, computed at DFT(B3LYP)/6-311++G(*d*,*p*) level in water and benzene solutions

Parameter	DMPO-$^{\bullet}R_i$										
	in water solution						in benzene solution				
	$^{\bullet}H$	$^{\bullet}N_3$	$^{\bullet}NH_2$	$^{\bullet}CH_3$	$^{\bullet}CCl_3$	$^{\bullet}OOH$	$^{\bullet}F$	$^{\bullet}OH$	$^{\bullet}CF_3$	$^{\bullet}CH_2OH$	$^{\bullet}OC_2H_5$
Dihedral angles (deg)											
N9–C1–C4–C3	28.4	−31.4	29.5	31.6	−20.3	−19.8	−30.3	−29.5	−23.9	30.1	32.1
C1–N9–C2–C3	−10.1	5.91	−8.5	−5.0	16.0	19.0	5.91	6.8	14.3	−7.4	−4.7
O18–N9–C2–C10	−70.6	−45.6	−74.9	−73.3	−63.5	−39.8	−56.1	−49.3	−61.9	−76.2	−61.9
C1–N9–C2–C10	108.5	125.5	110.0	113.7	136.5	138.6	125.9	126.8	134.5	111.3	113.8
O18–N9–C2–C11	50.8	75.8	46.6	48.0	57.4	81.9	65.1	71.9	59.2	44.9	59.3
O18–N9–C1–$^{\bullet}R_i$	45.3	−46.4	49.9	45.6	78.0	−60.8	80.3	73.3	80.3	49.0	−85.5
C2–N9–C1–$^{\bullet}R_i$	−133.7	142.3	−134.8	−141.4	−122.1	120.6	−101.7	−102.8	−116.0	−138.5	98.7
Bond angles (deg)											
C1–C4–C3	103.7	103.5	104.0	104.1	105.7	104.8	103.7	104.3	104.5	104.0	103.9
C2–C3–C4	105.4	105.7	105.4	105.4	105.6	105.5	105.2	105.5	105.5	105.5	105.2
C3–C2–C11	113.2	112.7	113.2	113.0	112.2	112.6	112.6	112.6	112.5	113.3	113.4
C3–C2–C10	112.4	113.0	112.4	112.5	113.7	113.2	113.5	113.3	113.5	112.5	112.4
C3–C2–N9	101.1	101.2	100.9	101.3	101.6	100.5	101.1	101.0	101.4	101.2	101.2
C4–C1–$^{\bullet}R_i$	114.4	116.5	114.0	115.9	114.8	114.0	110.0	109.6	113.2	115.8	108.5
C4–C1–N9	103.2	102.6	102.4	101.8	103.2	104.1	103.7	102.5	103.6	102.5	102.1
C11–C2–C10	110.7	110.7	110.7	110.7	110.8	110.9	110.9	108.6	110.9	110.6	110.7
O18–N9–C1	122.6	122.1	121.6	122.7	121.5	121.9	122.5	121.7	121.6	122.5	122.7
O18–N9–C2	123.1	123.3	123.5	122.4	120.9	123.7	123.1	123.4	122.2	122.6	122.7
Bond lengths (Å)											
N9–O18	1.275	1.271	1.274	1.275	1.272	1.272	1.271	1.273	1.270	1.273	1.275
C1–C4	1.530	1.530	1.527	1.531	1.541	1.529	1.516	1.523	1.537	1.531	1.524
C4–C3	1.542	1.538	1.540	1.539	1.541	1.541	1.542	1.543	1.542	1.540	1.541
C3–C2	1.543	1.545	1.544	1.544	1.536	1.541	1.545	1.544	1.540	1.543	1.544
C2–C11	1.530	1.536	1.530	1.531	1.537	1.538	1.536	1.537	1.537	1.530	1.531
C2–C1	2.492	2.499	2.501	2.505	2.504	2.487	2.474	2.499	2.494	2.499	2.497
C2–N9	1.496	1.500	1.495	1.498	1.505	1.498	1.501	1.470	1.502	1.497	1.497
	1.091	1.472	1.458	1.522	1.552	1.440	1.419	1.419	1.530	1.523	1.416
		N–N	N–H	C–H	C–Cl	O–O		O–H	C–F	O–H	C–H
C1–$^{\bullet}R_i$		1.231	1.016	1.093	1.803	1.450		0.970	1.270	0.962	1.093
		1.132	1.016	1.091	1.800	O–H			1.356		C–C
				1.093	1.812	0.989			1.343		1.523
C4–H7	1.090	1.089	1.093	1.095	1.089	1.090	1.089	1.090	1.089	1.094	1.092
C11–H17	1.092	1.092	1.092	1.093	1.092	1.093	1.092	1.093	1.092	1.093	1.093
C10–H14	1.091	1.091	1.092	1.092	1.092	1.091	1.091	1.091	1.091	1.092	1.091

Table 2. The hfcc's and energies (E) for the optimized structures of all the radical products of DMPO in water solution, and the binding energies (E_b, BSSE corrected, kcal/mol) of the radicals

DMPO–$^{\bullet}R_i$	Method		Hyperfine coupling constants, G					$-E$, hartree/part.	E_b
			C1	H_β20	N9	O18	$^{\bullet}R_i$		
	Exp. [3]			22.5	16.6		–		
DMPO–H	DFT/B3LYP	6-311++G(*d*,*p*)	–7.45	24.71	8.60	–10.02	a_H = 14.20	365.891438	96.57
		LanL2DZ	–7.82	22.78	16.03	–26.52	a_H = 13.71	365.737994	101.58
	DFT/B3PW91	6-311++G(*d*,*p*)	–7.55	24.90	7.12	–6.85	a_H = 14.21	365.753930	97.19
		LanL2DZ	–7.96	23.01	15.57	–25.34	a_H = 13.78	365.610964	101.58
	DFT/PBEPBE	6-311++G(*d*,*p*)	–6.73	26.76	5.88	–3.78	a_H = 15.09	365.423150	88.41
		LanL2DZ	–6.96	24.15	12.78	–19.26	a_H = 14.37	365.280031	90.30
	HF	6-311++G(*d*,*p*)	–15.76	22.73	23.41	–37.94	a_H = 13.61	363.548093	116.63
		LanL2DZ	–15.12	19.91	29.57	–59.29	a_H = 12.90	363.355694	110.99
	Exp. [3]			14.2	14.8		3.1 ^{14}N		
DMPO–N_3	DFT/B3LYP	6-311++G(*d*,*p*)	–6.76	19.54	8.25	–10.41	a_N = 2.5 a_N = 0.01 a_N = 0.02	529.519032	66.47
		LanL2DZ	–6.12	9.71	14.01	–28.16	a_N = 3.44 a_N = –0.16 a_N = 0.21	529.273110	55.18
	DFT/B3PW91	6-311++G(*d*,*p*)	–4.02	8.06	6.26	–6.95	a_N = 4.19 a_N = –0.22 a_N = 0.12	529.317949	55.81
		LanL2DZ	–4.58	7.46	13.68	–26.45	a_N = 3.60 a_N = –0.32 a_N = 0.69	529.081726	55.18
	DFT/PBEPBE	6-311++G(*d*,*p*)	–5.89	19.98	5.32	–3.94	a_N = 3.19 a_N = 0.06 a_N = 0.04	528.899210	63.33
		LanL2DZ	–0.97	6.79	11.32	–19.71	a_N = 4.55 a_N = –0.17 a_N = 0.84	528.679054	50.79
	HF	6-311++G(*d*,*p*)	–13.85	18.25	20.30	–40.01	a_N = 1.92 a_N = 0.04 a_N = –0.29	526.270122	75.25
		LanL2DZ	–12.13	9.34	20.52	63.29	a_N = 0.96 a_N = 0.96 a_N = –1.15	525.954348	68.97
	Exp. [3]			19.03	15.85		1.71^{14}N		
DMPO–NH_2	DFT/B3LYP	6-311++G(*d*,*p*)	–6.94	21.19	8.49	–10.24	a_N = 1.36 a_H = –0.48 a_H = –0.38	421.264847	89.04
		LanL2DZ	–6.27	16.41	15.94	–26.89	a_N = 1.46 a_H = –0.43 a_H = 0.01	421.086702	94.06
	DFT/B3PW91	6-311++G(*d*,*p*)	–7.12	21.95	7.21	–6.99	a_N = 1.27 a_H = –0.49 a_H = –0.36	421.111242	89.04
		LanL2DZ	–6.37	17.05	15.95	–25.32	a_N = 1.39 a_H = –0.43 a_H = 0.04	420.944690	96.57
	DFT/PBEPBE	6-311++G(*d*,*p*)	–6.16	24.15	5.87	–3.98	a_N = 1.16 a_H = –0.44 a_H = –0.31	420.738680	84.03

Table 2. (Contd.)

DMPO–•R_i	Method		Hyperfine coupling constants, G					$-E$, hartree/part.	E_b
			C1	H_β20	N9	O18	•R_i		
		LanL2DZ	−5.08	15.96	12.89	−19.49	$a_N = 1.38$ $a_H = -0.48$ $a_H = 0.01$	420.568526	87.79
	HF	6-311++G(*d*,*p*)	−14.43	10.63	22.86	−38.31	$a_N = 1.98$ $a_H = -1.23$ $a_H = -1.34$	418.604391	85.28
		LanL2DZ	−13.27	16.07	28.10	−60.56	$a_N = 1.41$ $a_H = -0.48$ $a_H = -0.17$	418.376922	108.48
	Exp. [3]			23.4	16.4		–		
DMPO–CH_3	DFT/B3LYP	6-311++G(*d*,*p*)	−6.18	24.43	9.04	−10.09	$a_C = 5.30$ $a_H = -0.20$ $a_H = -0.61$ $a_H = -0.54$	405.221205	97.19
		LanL2DZ	−7.12	22.68	16.29	−26.38	$a_C = 5.41$ $a_H = -0.32$ $a_H = -0.65$ $a_H = -0.61$	405.051032	99.70
	DFT/B3PW91	6-311++G(*d*,*p*)	−6.46	24.51	7.50	−6.93	$a_C = 5.34$ $a_H = -0.26$ $a_H = -0.61$ $a_H = -0.60$	405.069343	100.96
		LanL2DZ	−7.33	22.87	15.87	−25.20	$a_C = 5.44$ $a_H = -0.37$ $a_H = -0.68$ $a_H = -0.63$	404.911131	104.72
	DFT/PBEPBE	6-311++G(*d*,*p*)	−5.31	25.63	6.21	−3.92	$a_C = 5.86$ $a_H = -0.11$ $a_H = -0.46$ $a_H = -0.53$	404.693976	92.80
		LanL2DZ	−6.15	24.08	12.99	−19.17	$a_C = 5.73$ $a_H = -0.49$ $a_H = -0.16$ $a_H = -0.54$	404.537667	96.57
	HF	6-311++G(*d*,*p*)	−14.67	22.85	23.97	−37.69	$a_C = 5.30$ $a_H = -0.82$ $a_H = -1.71$ $a_H = -1.07$	402.597373	112.87
		LanL2DZ	−14.96	20.71	30.70	−58.62	$a_C = 5.15$ $a_H = -1.02$ $a_H = -2.06$ $a_H = -0.19$	402.383387	124.16
	Exp. [3]			14.6	14.6		–		
DMPO–CCl_3	DFT/B3LYP	6-311++G(*d*,*p*)	−6.13	12.05	9.09	−10.67	$a_C = 21.23$ $a_{Cl} = 0.12$ $a_{Cl} = 0.06$ $a_{Cl} = 0.04$	1784.065418	67.09
		LanL2DZ	−6.49	11.20	15.28	−28.14	$a_C = 21.01$ $a_{Cl} = 0$ $a_{Cl} = 0$ $a_{Cl} = 0$	448.043713	78.38

Table 2. (Contd.)

DMPO–•R$_i$	Method		Hyperfine coupling constants, G					$-E$, hartree/part.	E_b
			C1	H_β20	N9	O18	•R$_i$		
	DFT/B3PW91	6-311++G(*d*,*p*)	−6.88	20.01	6.86	−6.92	$a_C = 13.66$ $a_{Cl} = -0.17$ $a_{Cl} = 0.05$ $a_{Cl} = -0.08$	1783.754750	74.62
		LanL2DZ	−6.68	11.41	14.72	−26.88	$a_C = -21.58$ $a_{Cl} = 0$ $a_{Cl} = 0$ $a_{Cl} = 0$	447.968662	79.64
	DFT/PBEPBE	6-311++G(*d*,*p*)	−5.37	12.54	6.36	−4.28	$a_C = 29.64$ $a_{Cl} = 0.29$ $a_{Cl} = -0.07$ $a_{Cl} = 0.30$	1782.964360	62.70
		LanL2DZ	−5.54	11.36	12.16	−20.40	$a_C = 35.08$ $a_{Cl} = 0$ $a_{Cl} = 0$ $a_{Cl} = 0$	447.544693	70.86
	HF	6-311++G(*d*,*p*)	−12.33	10.58	19.22	−40.54	$a_C = 12.64$ $a_{Cl} = -0.22$ $a_{Cl} = 0.06$ $a_{Cl} = -0.20$	1779.344385	89.67
		LanL2DZ	−10.92	8.60	20.29	−64.15	$a_C = 21.45$ $a_{Cl} = 0$ $a_{Cl} = 0$ $a_{Cl} = 0$	444.695396	106.60
	Exp. [3]			11.7	14.3		–		
DMPO–OOH	DFT/B3LYP	6-311++G(*d*,*p*)	−6.21	16	7.39	−10.53	$a_O = -7.82$ $a_O = -0.11$ $a_H = -0.01$	516.298303	54.55
		LanL2DZ	−5.60	8.99	13.91	−27.95	$a_O = -0.26$ $a_O = -5.48$ $a_H = 0.01$	516.096967	48.91
	DFT/B3PW91	6-311++G(*d*,*p*)	−5.19	7.09	5.72	−7.21	$a_O = -13.42$ $a_O = -0.67$ $a_H = -0.009$	516.102110	50.16
		LanL2DZ	−5.35	7.05	12.77	−27.21	$a_O = -11.17$ $a_O = -0.77$ $a_H = 0.001$	515.907237	48.91
	DFT/PBEPBE	6-311++G(*d*,*p*)	−3.92	6.91	4.27	−4.09	$a_O = -19.46$ $a_O = -2.50$ $a_H = -0.20$	515.684682	46.40
		LanL2DZ	−3.59	7.00	10.09	−20.49	$a_O = -15.44$ $a_O = -1.62$ $a_H = -0.63$	515.502496	43.26
	HF	6-311++G(*d*,*p*)	−13.59	5.11	18.36	−41.17	$a_O = -5.56$ $a_O = 0.45$ $a_H = 0.08$	513.217608	63.96
		LanL2DZ	−12.37	10.64	21.21	−64.36	$a_O = -3.46$ $a_O = 0.41$ $a_H = 0.06$	512.965627	63.96

Table 3. Hfcc's and energies for the optimized structures of all the radical products of DMPO in benzene solution, and the binding energies of the radicals

	Method		Hyperfine coupling constants (G)					$-E$, hartree/part.	E_b, kcal/mol
			Cl	$H_\beta 20$	N9	O18	$^\bullet R_i$		
	Exp. [3]			–	10.83		21.6 ^{19}F		
DMPO–F	DFT/B3LYP	6-311++G(*d*,*p*)	–3.07	4.25	6.09	–10.88	$a_F = 54.69$	465.160914	89.67
		LanL2DZ	–2.28	3.90	11.44	–29.70	$a_F = 53.37$	464.986378	87.16
	DFT/B3PW91	6-311++G(*d*,*p*)	–3.18	4.21	4.88	–7.22	$a_F = 54.32$	464.986282	90.92
		LanL2DZ	–2.45	3.97	10.99	–28.38	$a_F = 52.80$	464.819872	84.03
	DFT/PBEPBE	6-311++G(*d*,*p*)	–1.20	3.99	3.86	–4.12	$a_F = 65.04$	464.607031	95.31
		LanL2DZ	0.42	3.54	9.00	–21.58	$a_F = 65.92$	464.444076	87.16
	HF	6-311++G(*d*,*p*)	–10.43	4.33	14.48	–42.42	$a_F = 35.62$	462.434115	93.43
		LanL2DZ	–8.28	3.77	15.06	–66.24	$a_F = 30.07$	462.218141	80.89
DMPO–OH	Exp. [3]			12.1	13.7		–		
	DFT/B3LYP	6-311++G(*d*,*p*)	–4.35	6.08	7.49	–10.55	$a_O = -4.95$ $a_H = -0.81$	441.139141	79.01
		LanL2DZ	–4.32	5.29	13.99	–28.38	$a_O = -4.93$ $a_H = -0.80$	440.951502	73.99
	DFT/B3PW91	6-311++G(*d*,*p*)	–5.06	6.48	6.06	–7.10	$a_O = -4.94$ $a_H = -0.80$	440.972069	80.26
		LanL2DZ	–4.98	5.73	13.28	–27.20	$a_O = -5.04$ $a_H = -0.79$	440.791678	75.87
	DFT/PBEPBE	6-311++G(*d*,*p*)	–3.78	16.80	6.36	–3.94	$a_O = -1.09$ $a_H = -0.37$	440.596378	89.67
		LanL2DZ	–2.65	13.95	13.51	–20.22	$a_O = -1.35$ $a_H = -0.55$	440.421018	84.03
	HF	6-311++G(*d*,*p*)	–11.49	6.08	18.48	–41.00	$a_O = -4.43$ $a_H = -1.07$	438.433322	84.03
		LanL2DZ	–11.11	5.45	20.79	– 64.44	$a_O = -4.17$ $a_H = -0.68$	438.202172	80.26
DMPO–CF_3	Exp. [3]			13.22	15.54		–		
	DFT/B3LYP	6-311++G(*d*,*p*)	–6.17	11.60	8.26	–10.78	$a_C = 14.62$ $a_F = 1.67$ $a_F = 0.34$ $a_F = 0.79$	703.035127	77.75
		LanL2DZ	–7.05	10.20	13.86	–29.11	$a_C = 13.73$ $a_F = 2.52$ $a_F = 0.64$ $a_F = 0.92$	702.782446	82.14
	DFT/B3PW91	6-311++G(*d*,*p*)	–6.32	11.92	6.88	–7.20	$a_C = 14.87$ $a_F = 1.75$ $a_F = 0.09$ $a_F = 0.96$	702.771001	68.97
		LanL2DZ	–6.96	10.56	13.38	–27.77	$a_C = 14.22$ $a_F = 2.64$ $a_F = 0.44$ $a_F = 1.15$	702.528413	84.03
	DFT/PBEPBE	6-311++G(*d*,*p*)	–5.36	12.49	5.89	–4.18	$a_C = 16.52$ $a_F = 0.36$ $a_F = 2.52$ $a_F = 1.31$	702.256770	72.11
		LanL2DZ	–5.97	11.00	11.30	–21.13	$a_C = 16.83$ $a_F = 4.37$ $a_F = 0.74$ $a_F = 1.51$	702.021304	75.87

Table 3. (Contd.)

	Method		Hyperfine coupling constants (G)					$-E$, hartree/part.	E_b, kcal/mol
			Cl	$H_\beta 20$	N9	O18	$^\bullet R_i$		
	HF	6-311++G(*d*,*p*)	−11.90	9.82	17.23	−41.51	$a_C = 10.92$ $a_F = -0.11$ $a_F = -0.64$ $a_F = 0.005$	699.262205	97.82
		LanL2DZ	−10.53	7.47	17.72	−65.30	$a_C = 7.80$ $a_F = -0.17$ $a_F = -0.22$ $a_F = 0.38$	698.946681	109.11
	Exp. [3]			20.67	14.66				
DMPO–CH_2OH	DFT/B3LYP	6-311++G(*d*,*p*)	−6.06	22.42	8.22	−10.37	$a_C = 5.93$ $a_H = -0.46$ $a_H = -0.48$ $a_O = 0.09$ $a_H = 0.26$	480.453228	91.55
		LanL2DZ	−6.76	12.56	14.76	−27.76	$a_C = 10.17$ $a_H = -0.83$ $a_H = -0.57$ $a_O = -0.26$ $a_H = -0.07$	480.249413	76.50
	DFT/B3PW91	6-311++G(*d*,*p*)	−5.51	17.53	7.69	−6.95	$a_C = 8.02$ $a_H = -0.62$ $a_H = -0.65$ $a_O = -0.01$ $a_H = -0.03$	480.273038	79.64
		LanL2DZ	−7.21	21.37	14.48	−26.37	$a_C = 5.95$ $a_H = -0.55$ $a_H = -0.49$ $a_O = 0.02$ $a_H = 0.38$	480.078451	69.60
	DFT/PBEPBE	6-311++G(*d*,*p*)	−4.39	19.21	6.81	−4.00	$a_C = 8.75$ $a_H = -0.51$ $a_H = -0.47$ $a_O = -0.006$ $a_H = 0.02$	479.858604	74.62
		LanL2DZ	−5.97	20.98	11.88	−20.03	$a_C = 6.98$ $a_H = -0.38$ $a_H = -0.39$ $a_O = -0.14$ $a_H = -0.09$	479.664906	77.75
	HF	6-311++G(*d*,*p*)	−12.63	14.90	20.34	−39.78	$a_C = 7.14$ $a_H = -1.07$ $a_H = -1.55$ $a_O = 0.26$ $a_H = 0.11$	477.470585	98.45
		LanL2DZ	−13.39	12.94	26.01	−61.52	$a_C = 7.77$ $a_H = -1.29$ $a_H = -0.6$ $a_O = 0.38$ $a_H = 0.12$	477.220119	104.09
	Exp. [3]			11.09	14.06				
DMPO–OC_2H_5	DFT/B3LYP	6-311++G(*d*,*p*)	−5.79	4.27	7.46	−10.75	$a_O = -5.81$ $a_C = -0.45$ $a_H = 0.76$ $a_H = 0.81$ $a_C = 0.45$ $a_H = -0.06$ $a_H = 0.28$ $a_H = 0.18$	519.772037	65.21

Table 3. (Contd.)

Method		Hyperfine coupling constants (G)					$-E$, hartree/part.	E_b, kcal/mol
		Cl	$H_\beta 20$	N9	O18	$^\bullet R_i$		
	LanL2DZ	−6.03	4.71	13.70	−28.46	$a_O = -5.01$ $a_C = -0.51$ $a_H = 0.77$ $a_H = 1.48$ $a_C = 0.07$ $a_H = 0.19$ $a_H = 0.15$ $a_H = -0.05$	519.554524	62.70
DFT/B3PW91	6-311++G(*d*,*p*)	−5.72	12.74	6.24	−7.08	$a_O = -3.27$ $a_C = -0.42$ $a_H = 0.28$ $a_H = 0.63$ $a_C = 0.31$ $a_H = 0.25$ $a_H = 0.15$ $a_H = -0.04$	519.574652	75.25
	LanL2DZ	−5.77	10.14	13.65	−27.12	$a_O = -3.65$ $a_C = -0.36$ $a_H = 0.12$ $a_H = 0.67$ $a_C = 0.55$ $a_H = 0.26$ $a_H = 0.11$ $a_H = -0.07$	519.369426	69.60
DFT/PBEPBE	6-311++G(*d*,*p*)	−4.34	4.43	4.94	−4.04	$a_O = -6.92$ $a_C = -0.38$ $a_H = 1.11$ $a_H = 0.04$ $a_C = 0.42$ $a_H = -0.01$ $a_H = -0.08$ $a_H = 0.26$	519.115303	63.33
	LanL2DZ	−3.49	9.15	11.61	−20.57	$a_O = -4.11$ $a_C = -0.34$ $a_H = 0.25$ $a_H = 1.22$ $a_C = 0.77$ $a_H = 0.34$ $a_H = 0.16$ $a_H = -0.06$	518.914591	65.21
HF	6-311++G(*d*,*p*)	−13.74	13.24	18.90	−40.60	$a_O = -2.64$ $a_C = -0.50$ $a_H = 0.20$ $a_H = 0.21$ $a_C = 0.11$ $a_H = 0.12$ $a_H = 0.06$ $a_H = -0.04$	516.507893	85.91
	LanL2DZ	−11.72	5.10	21.19	−64.16	$a_O = -4.43$ $a_C = -0.41$ $a_H = 0.66$ $a_H = 0.24$ $a_C = -0.31$ $a_H = -0.01$ $a_H = -0.06$ $a_H = 0.08$	516.233317	72.11

Table 4. Hfcc's due to the β proton of the nitrogen and the angle between P_π orbital of nitrogen and projection of the CH bond to the P_π orbital plane calculated at the DFT (B3LYP)/6-311++G(*d*,*p*) for all the radical products of DMPO

DMPO/•R	θ (deg)	$\alpha_\beta(H_2O)$, G	$\cos^2\theta$
Water			
•H	17.09	24.71	0.913
$•N_3$	21.46	19.54	0.866
$•NH_2$	17.83	21.19	0.906
$•CH_3$	15.63	24.43	0.927
$•CCl_3$	52.24	12.05	0.374
•OOH	34.50	16.00	0.679
Benzene			
•F	54.25	4.25	0.341
•OH	42.17	6.08	0.549
$•CF_3$	53.65	11.60	0.351
$•CH_2OH$	20.46	22.42	0.877
$•OC_2H_5$	53.07	4.27	0.361

vided that their respective nucleus spin densities have opposite sign.

The variation of the hfcc's due to the β proton, H20, of the nitroxide radical, N9, with the angle θ between the P_π orbital of the nitrogen and the projection of the C1–H20 bond to the P_π orbital plane has been found as $\alpha_\beta = -3.018 + 27.96\cos^2\theta$ with a 0.83 value of R^2. The computed α_β and θ's at the DFT(B3LYP)/6-311++G(*d*,*p*) level for all the radical products can be seen in Table 4. The θ's have been obtained by the help of the dihedral angle of O18–N9–C1–H20 (see Fig. 2). In here we have used together the calculated hfcc's of the β proton (α_β) in the different solutions since it was experimentally found that the hfcc due to the β proton of nitro radical anion was insensitive with solvent change [16]. When we have compared the obtained equation of $\alpha_\beta = -3.018 + 27.96\cos^2\theta$ with the McConnell relation of $\alpha_\beta = B_0 + B_1\cos^2\theta$ where B_0, as we mentioned before, is the spin polarization contribution (0–3.5) and B_1 the hyper conjugative contribution (~50) [1]. It is seen that the value of B_0 is almost agree, but B_1 is somewhat low. This can be attributed to the opposite spin density of the oxygen nucleus ($\alpha_{O18} \sim -28$ G) bonded to the nitrogen N9. This comment has also been given in our previous study [7]. So we state that the Mc Connell equation is also valid for the radical products in different environments.

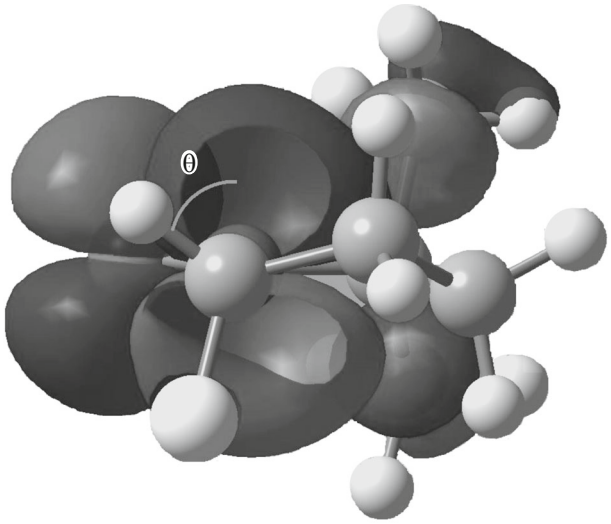

Fig. 2. Angle (θ) between the P_π orbital of the nitrogen and the projection of CH bond to the P_π orbital plane.

As an example, at the DFT(B3LYP)/6-311++G(*d*,*p*) level the highest single occupied molecular orbital SOMO (such as half-filled HOMO of a radical) and lowest unoccupied molecular orbital (LUMO) graphs and, some energy levels for the DMPO/•F spin adduct have been given in Fig. 3. The NPA charges, Mulliken charges and Mulliken spin densities of the N9 and O18 atoms and, the SOMO–LUMO energy gap (Δ*E*) values calculated at the DFT(B3LYP)/6-311++G(*d*,*p*) level for all the DMPO/•R spin adducts have been given in Table 5. The SOMO–LUMO energy gap (Δ*E*) is heavily dependent on the trapped radical. The smaller gap between the SOMO and LUMO orbitals characterizes their lower molecular chemical stability [17]. As seen, the SOMO–LUMO gap for the DMPO/$•N_3$ spin adduct is lowest while it is highest for the DMPO/•F spin adduct. From this table it can also be concluded that the spin density on the N atom decreases while the one of the O atom increases, and this causes a lower hfcc for the β proton. This comment can easily be understood from Table 6.

In order to understand the intra-molecular interactions, the stabilization energies of all the DMPO/•R spin adducts were investigated by using second-order perturbation theory. The stabilization energy value is a variable depending on donor orbital occupancy, donor-acceptor orbital energy and, NBO Fock-Matrix element. The strong intra-molecular hyper conjugative interactions have been found at intra-molecular charge transfers (ICT) from the lone pair *n* electrons of O18 atom to the σ* anti-bonding orbitals of C1–N9 and C2–N9. The strongest hyper conjugative interaction is between the lone pair O18 atom and

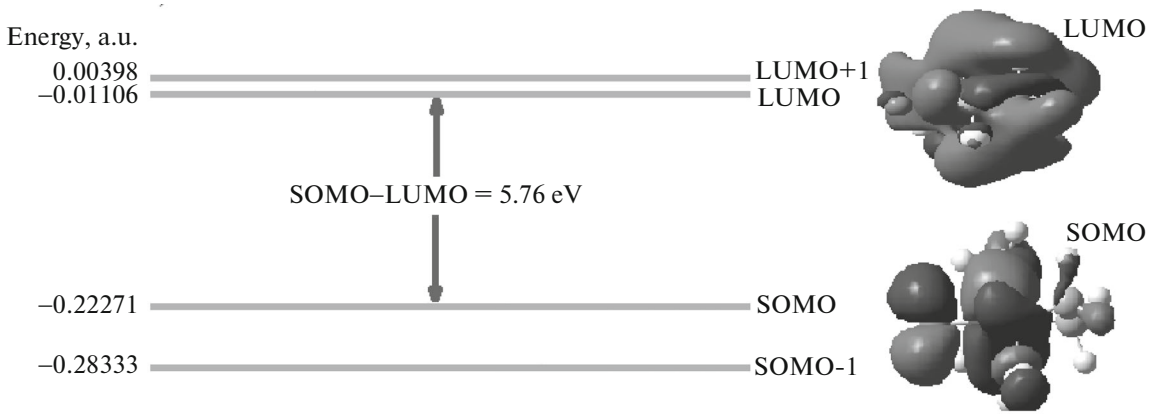

Fig. 3. SOMO and LUMO orbital forms and some energy levels of the DMPO/•F-spin adduct.

σ*(C2–N9), and the stabilizations energy of this interaction is 6.30 kcal mol^{-1}.

CONCLUSIONS

The optimized ground state structures of some radical adducts of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) in water and benzene solutions have theoretically been determined. Between the computations at the DFT(B3LYP, B3PW91, and PBEPBE) and HF/6-311++G(*d*,*p*), and LanL2DZ levels, the DFT(B3PW91)/LanL2DZ level was found to give more suitable values than the other levels for the hyperfine calculations. As selected radicals •H, •N_3, •NH_2, •CH_3, •CCl_3, •OOH in water and •F, •OH, •CF_3, •CH_2OH, •OC_2H_5 in benzene solutions were used. Also the calculated geometrical parameters (bond length, bond angle and torsion angle) for all the radical products have been listed, and the binding energies of all the trapped radicals have been obtained. The most tight-binding radical has been found as •H while the most lost-binding radical is •OOH. The hfcc due to the β proton of the nitroxide radical was found

Table 5. Mulliken atomic spin densities (ρ), charges (*q*), NPA atomic charge (q_1), and SOMO–LUMO energy gap (E_g, eV) calculated at the DFT(B3LYP)/6-311++G(*d*,*p*) level

DMPO/•R	ρ		*q*		q_1		E_g
	N9	O18	N9	O18	N9	O18	
Water							
•H	0.5007	0.4609	0.0679	–0.2335	0.2572	–0.0210	5.284
•N_3	0.4689	0.4951	0.2123	–0.2070	0.2272	0.0164	4.475
•NH_2	0.4998	0.4694	0.1460	–0.2402	0.2485	–0.0113	5.393
•CH_3	0.5127	0.4574	0.1746	–0.2347	0.2539	–0.0184	5.279
•CCl_3	0.4519	0.5120	0.0925	0.1976	0.2168	0.0360	4.598
•OOH	0.4681	0.4966	0.0571	–0.1685	0.2152	0.0321	5.515
Benzene							
•F	0.4060	0.5437	–0.0265	–0.0961	0.1822	0.0721	5.759
•OH	0.4561	0.5053	0.0303	–0.1366	0.2121	0.0322	5.411
•CF_3	0.4345	0.5338	0.0405	–0.0723	0.2091	0.0563	5.592
•CH_2OH	0.4733	0.4941	0.1584	–0.1409	0.2324	0.0168	5.127
•OC_2H_5	0.4536	0.5115	0.0430	–0.0961	0.2093	0.0340	5.364

Table 6. Mulliken atomic spin densities (ρ) and hfcc's due to the β proton of the nitrogen values (α_β) calculated at the DFT(B3LYP)/6-311++G(*d*,*p*) level

DMPO/•R	ρ		$\alpha_\beta(H_2O)$
	N9	O18	
$^\bullet CH_3$	0.5127	0.4574	24.71
$^\bullet H$	0.5007	0.4609	19.54
$^\bullet NH_2$	0.4998	0.4694	21.19
$^\bullet CH_2OH$	0.4733	0.4941	24.43
$^\bullet N_3$	0.4689	0.4951	12.05
$^\bullet OOH$	0.4681	0.4966	16.00
$^\bullet OH$	0.4561	0.5053	6.08
$^\bullet OC_2H_5$	0.4536	0.5115	4.27
$^\bullet CCl_3$	0.4519	0.5120	12.05
$^\bullet CF_3$	0.4345	0.5338	11.60
$^\bullet F$	0.4060	0.5437	4.25

to be consist with McConnel equation $\alpha_\beta = B_0 + B_1\cos^2\theta$. In this relationship it was found that the value of B_0 is almost agreed, but B_1 is somewhat low. This was attributed to the opposite spin density of the oxygen nucleus bonded to the nitrogen. The strong intramolecular hyper conjugation interactions have been obtained at the intra-molecular charge transfers (ICT) between the lone pair (O18) atom and the anti-bonding orbitals of σ*(C1–N9) and σ*(C2–N9).

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