NMR 13C SPECTRA
OF THE 1,1,3-TRIMETHYL-3-(4-METHYLPHENYL)BUTYL HYDROPEROXIDE IN VARIOUS SOLVENTS: MOLECULAR MODELING

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Abstract. GIAO-calculated NMR 13C chemical shifts as obtained at various computational levels are reported for the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide. The data are compared with experimental solution data in chloroform-d, acetonitrile-d_3, and DMSO-d_6, focusing on the agreement with spectral patterns and spectral trends. Calculation of magnetic shielding tensors and chemical shifts for 13C nuclei of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide molecule in the approximation of an isolated particle and considering the solvent influence in the framework of the continuum polarization model (PCM) was carried out. Comparative analysis of experimental and computer NMR spectroscopy results revealed that the GIAO method with MP2/6-31G(d,p) level of theory and the PCM approach can be used to estimate the NMR 13C chemical shifts of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide.

Key words: NMR spectroscopy, 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide, chemical shift, magnetic shielding constant, GIAO, molecular modeling.

Introduction

Arylalkyl hydroperoxides are useful starting reagents in the synthesis of surface-active peroxide initiators for the preparation of polymeric colloidal systems with improved stability [5]. Thermolysis of arylalkyl hydroperoxides was studied in acetonitrile [11]. NMR ^{1}H spectroscopy has been already used successfully for the experimental evidence of the complex formation between a 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide and tetraalkylammonium bromides in acetonitrile [2; 9; 12] and chloroform solution [9]. The aim of this work is a comprehensive study of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide (ROOH) by experimental NMR ^{13}C spectroscopy and molecular modeling methods.

Experimental

The 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide (ROOH) was purified according to [5]. Its purity (99 %) was controlled by iodometry method as well as by NMR spectroscopy. Experimental NMR ^{13}C spectra of the hydroperoxide solutions were obtained by using the Bruker Avance II 400 spectrometer (NMR ^{1}H – 400 MHz, NMR [13]C – 100 MHz) at 297 K. Solvents, chloroform-d, acetonitrile-d_3, and DMSO-d_6, were Sigma-Aldrich reagents and were used without additional purification but were stored above molecular sieves before using. Tetramethylsilane (TMS) was internal standard. The hydroperoxide concentration in solutions was 0.03 mol · dm^{-3}.

Molecular geometry and electronic structure parameters, as well as harmonic vibrational frequencies of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide molecule were calculated after full geometry optimization in the framework of B3LYP/6-31G(d,p) and MP2/6-31G(d,p) methods. The resulting equilibrium molecular geometry was used for total electronic energy calculations by the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) methods. All calculations have been carried out using the Gaussian03 [4] program.

The magnetic shielding tensors (c, ppm) for ^{13}C nuclei of the hydroperoxide and the reference molecule were calculated with the MP2/6-31G(d,p) and B3LYP/6-31G(d,p) equilibrium geometries by standard GIAO (Gauge-Independent Atomic Orbital) approach [13]. The calculated magnetic isotropic shielding tensors, χ_i, were transformed to chemical shifts relative to TMS molecule, δ_i, by $\delta_i = \chi_{ref} - \chi_i$, where both, χ_{ref} and χ_i, were taken from calculations at the same computational level. Table 1 illustrates c values for TMS molecule used for the hydroperoxide ^{13}C nuclei chemical shifts calculations.

χ values were also estimated in the framework of 6-311G(d,p) and 6-311++G(d,p) basis sets on the base of MP2/6-31G(d,p) and B3LYP/6-31G(d,p) equilibrium geometries. The solvent effect was considered in the PCM approximation [3; 7]. χ values for magnetically equivalent nuclei were averaged.

Inspecting the overall agreement between experimental and theoretical spectra RMS errors (σ) were used to consider the quality of the ^{13}C nuclei chemical shifts calculations. Correlation coefficients (R) were calculated to estimate the agreement between spectral patterns and trends.

Results and Discussions

Experimental NMR ^{13}C spectra of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide

Experimental NMR ^{13}C spectra of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide

Table 1

Magnetic shielding tensors for ^{13}C nuclei of the TMS

Solvent	MP2			B3LYP		
	1	2	3	1	2	3
-	207.54	199.71	199.37	191.80	184.13	183.72
Chloroform	207.86	200.13	199.79	192.08	184.53	184.13
Acetonitrile	208.01	200.32	199.99	192.19	184.70	184.30
DMSO	208.01	200.33	200.00	192.30	184.81	184.40

Note. 1 - 6-31G(d,p); 2 - 6-311G(d,p); 3 - 6-311++G(d,p).

(ROOH) were obtained from chloroform-d, acetonitrile-d$_3$, and DMSO-d$_6$ solutions. The hydroperoxide concentration in all samples was 0.03 mol · dm^{-3}. The experimental NMR ^{13}C spectra of the ROOH are presented in Fig. 1.
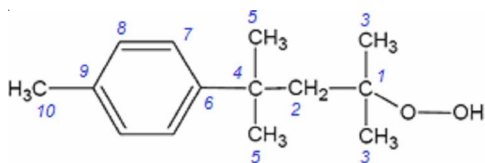
Ten signals for the hydroperoxide carbon atoms are observed in the ROOH ^{13}C NMR

spectrum. Signal of the carbon atom bonded with a hydroperoxide group shifts slightly to the stronger fields with the solvent polarity increasing, while the remaining signals are shifted to weak fields. A linear dependences between the ^{13}C chemical shifts values of the hydroperoxide are observed in the studied solvents (Fig. 1). This is consistent with the authors [1], who showed linear correlation between the chemical shifts values in chloroform-d and dimethylsulphoxide-d$_6$ for a large number of organic compounds of different
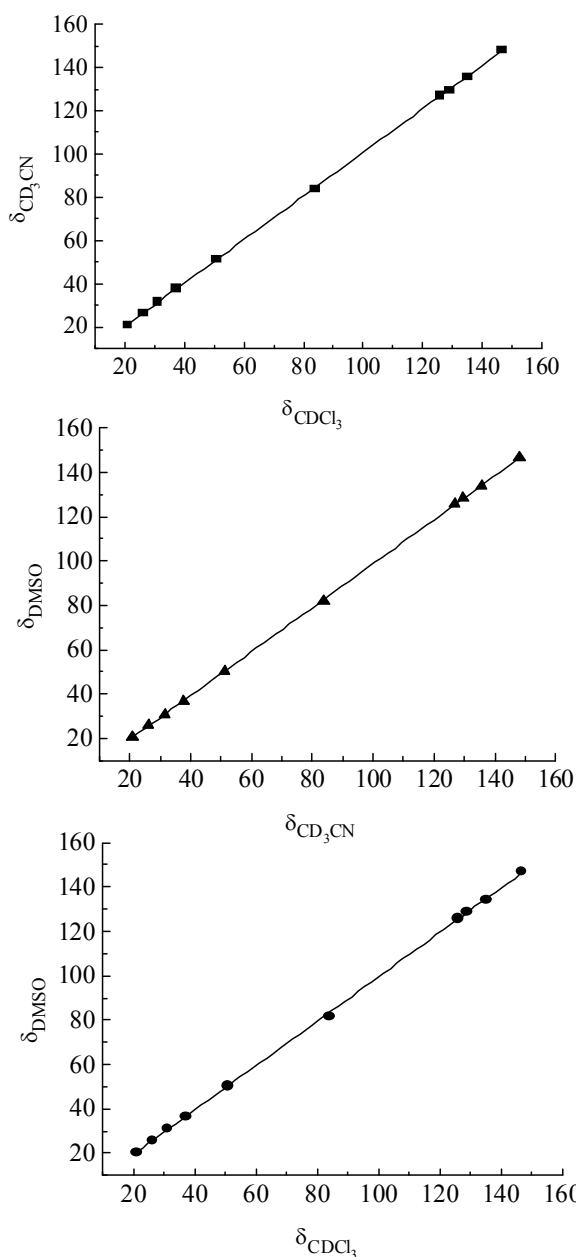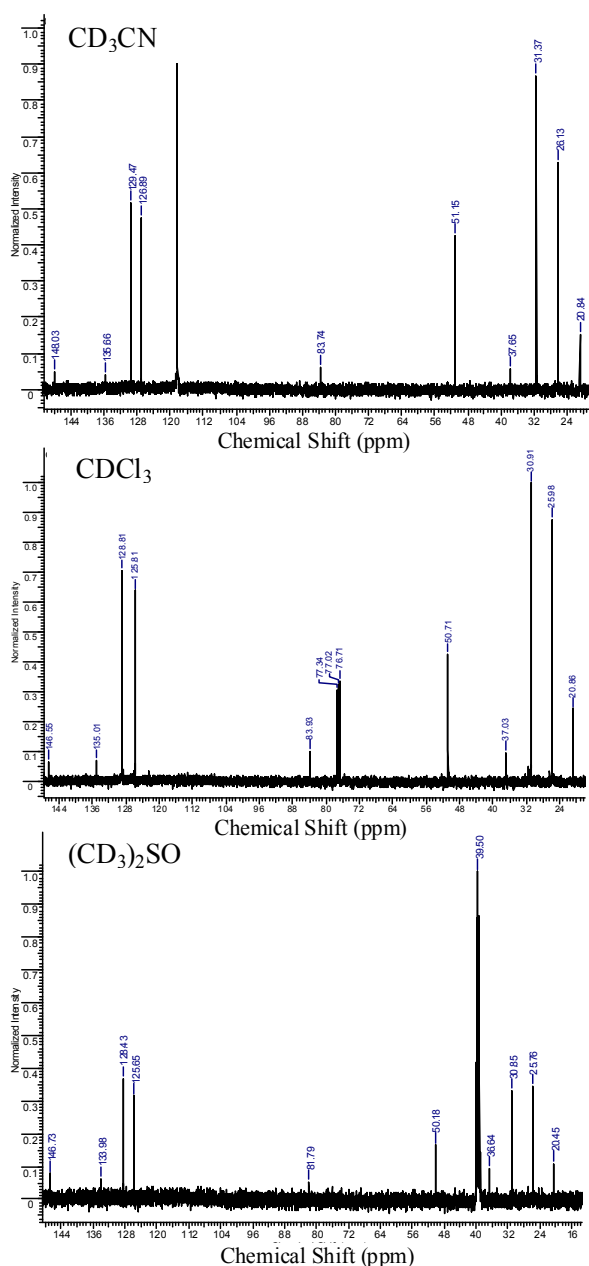

Fig. 1. The relationship between the *e*xperimental NMR ^{13}C chemical shifts (relative to TMS)
of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide in different solvents

classes. Equations corresponded to the obtained relationships (Fig. 1) are listed below.

$$\delta_{CD_3CN} = (0.02 \pm 0.23) + (1.006 \pm 0.002)\delta_{CDCl_3}$$

$$\delta_{DMSO-d_6} = (-0.46 \pm 0.41) + (0.999 \pm 0.004)\delta_{CDCl_3}$$

$$\delta_{DMSO-d_6} = (-0.48 \pm 0.24) + (0.993 \pm 0.003)\delta_{CD_3CN}$$

Molecular modeling of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide NMR ^{13}C spectra by MP2 and B3LYP methods

The hydroperoxide molecule geometry optimization in the framework of MP2/6-31G(d,p) and B3LYP/6-31G(d,p) methods was carried out as the first step of the hydroperoxide NMR ^{13}C spectra modeling. Initial hydroperoxide configuration chosen for calculations was the one obtained by semiempirical AM1 method and used recently for the hydroperoxide O-O bond homolysis [11] as well as complexation with Et_4NBr [2; 10] modeling. The main parameters of the hydroperoxide fragment molecular geometry obtained in the isolated particle approximation within

the framework of MP2/6-31G(d,p) (Fig. 2) and B3LYP/6-31G(d,p) levels of theory are presented in Table 2. Peroxide bond O-O is a reaction centre in this type of chemical initiators. Thus, the main attention was focused on the geometry of -CO-OH fragment. The calculation results were compared with known experimental values for the *tert*-butyl hydroperoxide [6], and appropriate agreement between calculated and experimental parameters can be seen in the case of MP2/6-31G(d,p) method.

Calculation of ^{13}C chemical shifts of the hydroperoxide was carried out by GIAO method in the approximation of an isolated particle as well as in studied solvents within the PCM model, which takes into account the nonspecific solvation. Equilibrium hydroperoxide geometries obtained in the framework of MP2/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory for the isolated particle approximation were used in all cases.

The chemical shift values (δ, ppm) for ^{13}C nuclei in the hydroperoxide molecule were evaluated on the base of calculated magnetic shielding constants (χ, ppm). TMS was used as
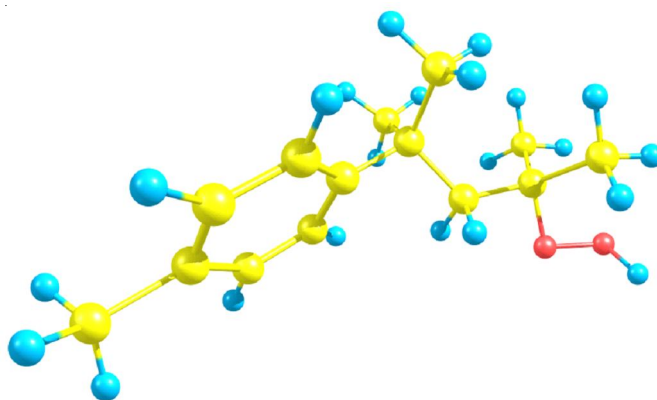
Fig. 2. The 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide structural model (MP2/6-31G(d,p) method)

Table 2

Molecular geometry parameters of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide -CO-OH moiety

Parameter	MP2/6-31G(d,p)	B3LYP/6-31G(d,p)	Experiment
l_{O-O}, Å	1.473	1.456	1.473
l_{C-O}, Å	1.459	1.465	1.443
l_{O-H}, Å	0.970	0.971	0.990
C-O-O, °	108.6	110.0	109.6
O-O-H, °	98.2	99.9	100.0
C-O-O-H, °	112.4	109.1	114.0

Note. Experimental values are those for *tert*-butyl hydroperoxide from [13].

standard, for which the molecular geometry optimization and χ calculation were performed using the same level of theory and basis set. Values of the ^{13}C chemical shifts were found as the difference of the magnetic shielding tensors of the corresponding TMS and hydroperoxide nuclei (Tables 3 and 4).

The correct spectral pattern for the hydroperoxide NMR ^{13}C spectrum was obtained for all methods and basis sets used within the isolated molecule approximation (see Table 3) as well as solvation accounting (see Table 4). Exceptions are aromatic C8 and C9 carbons, which signals are interchanged for all calculations.

The best reproduced experimental chemical shift value for the carbon atom of the CO-OH group is observed in the case of MP2/6-31G(d,p) approximation in all used solvents whereas B3LYP with the same basis set gives slightly worse values.

Basis set extension to 6-311++G(d,p) leads to a deterioration of the calculation results. Calculated value for the carbon of CO-OH group (83.61 ppm) within the isolated molecule approximation is closest to experimental one in acetonitrile (83.74 ppm). When passing to the calculations in the PCM mode solvation accounting leads to more correct results for the MP2 and B3LYP methods. The lowest σ values for all solvents are obtained with 6-31G(d,p) basis set. Linear relationships between the experimental NMR ^{13}C chemical shifts and the calculated values δ_{calc} for the hydroperoxide ^{13}C nuclei (see Fig. 3) have been obtained for both methods and all basis sets. The correlation coefficients (R) corresponding to obtained dependences are shown in Table 4. Joint account of σ and R values indicates possibility of MP2 method with 6-31G(d,p) basis set using for the calculation of the hydroperoxide ^{13}C nuclei chemical shifts.
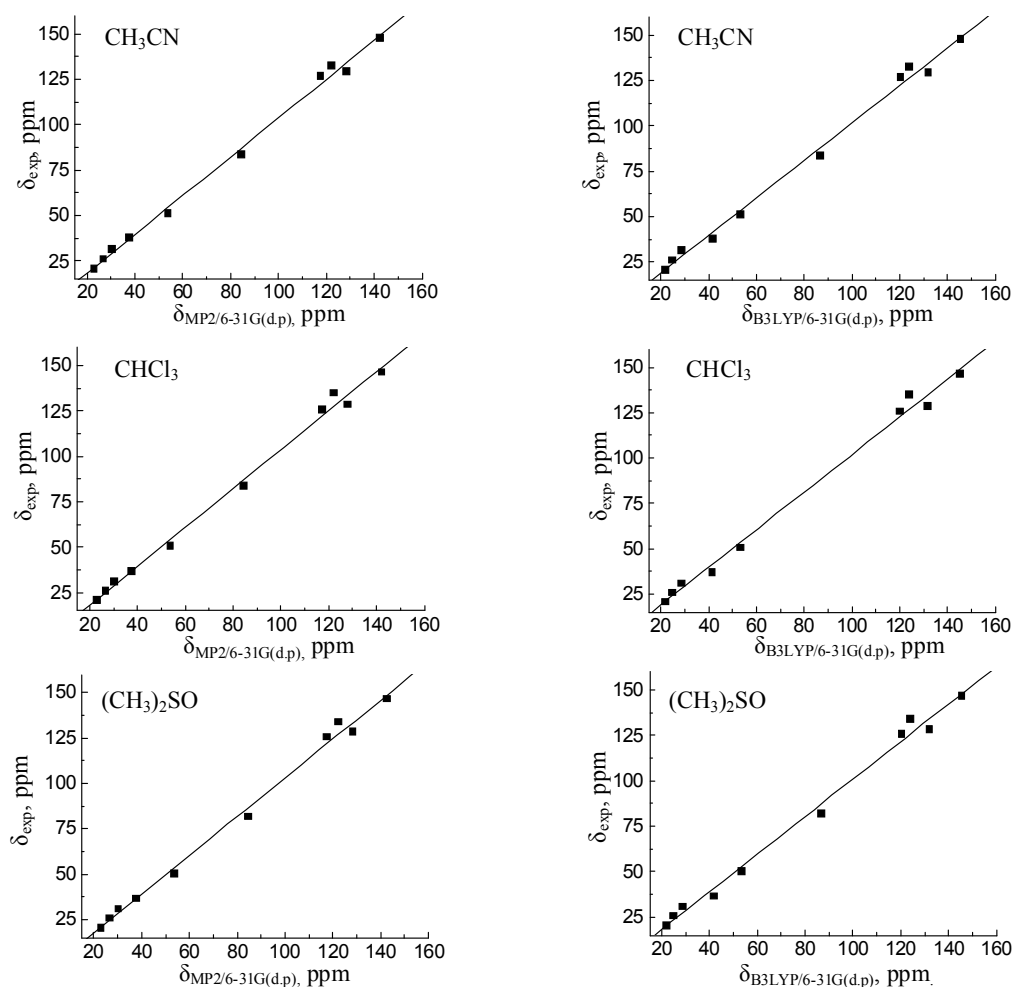

Fig. 3. Experimental (δ_{exp}) versus GIAO calculated ^{13}C chemical shifts (relative to TMS) of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide

Table 3

NMR ^{13}C chemical shifts (δ, ppm) of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide (the isolated particle approximation)

Nuclei	MP2			B3LYP		
	1	2	3	1	2	3
C1	83.61	86.87	88.24	85.77	90.90	92.04
C2	53.50	57.48	57.42	53.23	57.70	57.00
C3	26.46	26.71	26.62	24.62	25.27	24.93
C4	37.04	40.23	40.37	41.14	44.66	44.49
C5	30.10	30.93	31.03	28.57	29.78	29.75
C6	141.39	153.47	153.93	144.46	158.38	158.37
C7	116.91	125.90	126.29	119.80	130.58	131.03
C8	127.07	137.37	137.97	130.75	142.40	143.32
C9	121.55	130.79	131.41	123.68	134.44	135.07
C10	22.98	23.82	23.75	21.84	23.25	22.84

Note. 1 - 6-31G(d,p); 2 - 6-311G(d,p); 3 - 6-311++G(d,p).

Table 4

NMR ^{13}C chemical shifts (δ, ppm) of the 1,1,3-trimethyl-3-(4-methylphenyl)butyl hydroperoxide in different solvents

Nuclei	MP2			B3LYP			4
	1	2	3	1	2	3	
Chloroform							
C1	84.29	87.74	89.27	86.44	91.86	93.14	83.93
C2	53.69	57.73	57.64	53.37	57.89	57.17	50.71
C3	26.62	26.99	26.89	24.73	25.52	25.17	25.98
C4	37.46	40.74	40.92	41.54	45.20	45.07	37.03
C5	30.18	31.10	31.20	28.59	29.90	29.88	30.91
C6	142.14	154.40	154.90	145.12	159.23	159.25	146.55
C7	117.33	126.51	126.91	120.11	131.14	131.60	125.81
C8	127.92	138.43	139.03	131.56	143.43	144.34	128.81
C9	121.90	131.35	131.91	123.85	134.81	135.37	135.01
C10	23.01	23.96	23.88	21.81	23.36	22.93	20.86
σ	*27.86*	*25.63*	*28.66*	*20.82*	*59.16*	*63.32*	-
R	*0.997*	*0.997*	*0.997*	*0.996*	*0.996*	*0.996*	-
Acetonitrile							
C1	84.58	88.13	89.73	86.72	92.27	93.61	83.74
C2	53.80	57.88	57.78	53.44	57.98	57.27	51.15
C3	26.70	27.13	27.02	24.77	25.63	25.28	26.13
C4	37.64	40.99	41.18	41.71	45.43	45.32	37.65
C5	30.22	31.19	31.29	28.59	29.95	29.93	31.37
C6	142.50	154.84	155.37	145.42	159.62	159.66	148.03
C7	117.52	126.80	127.20	120.24	131.37	131.84	126.89
C8	128.29	138.90	139.49	131.88	143.85	144.75	129.47
C9	122.08	131.63	132.17	123.94	135.00	135.52	132.66
C10	23.03	24.04	23.96	21.80	23.41	22.97	20.84
σ	*24.571*	*22.325*	*25.741*	*17.395*	*55.560*	*60.243*	
R	*0.998*	*0.998*	*0.998*	*0.997*	*0.997*	*0.996*	
DMSO							
C1	84.60	88.15	89.75	86.84	92.38	93.72	81.79
C2	53.80	57.88	57.78	53.54	58.09	57.37	50.18
C3	26.70	27.13	27.03	24.87	25.74	25.37	25.76
C4	37.65	41.00	41.19	41.82	45.54	45.43	36.64
C5	30.22	31.19	31.30	28.69	30.06	30.03	30.85
C6	142.52	154.86	155.39	145.54	159.74	159.77	146.73
C7	117.53	126.81	127.22	120.35	131.48	131.94	125.65
C8	128.31	138.92	139.52	131.99	143.97	144.86	128.43
C9	122.09	131.64	132.18	124.05	135.11	135.62	133.98
C10	23.03	24.04	23.96	21.90	23.51	23.06	20.45
σ	*25.496*	*31.656*	*35.949*	*21.206*	*70.994*	*76.092*	
R	*0.997*	*0.997*	*0.997*	*0.995*	*0.996*	*0.995*	

Note. 1 - 6-31G(d,p); 2 - 6-311G(d,p); 3 - 6-311++G(d,p); 4 - experimental data.

Conclusions

A comprehensive study of the 1,1,3-trimethyl-3-(4-methyl-phenyl)butyl hydroperoxide by experimental NMR ^{13}C spectroscopy and molecular modeling methods was performed. A comparative assessment of the ^{13}C nuclei chemical shifts calculated by GIAO in various approximations. For NMR ^{13}C spectra of the hydroperoxide in different solvents MP2 and B3LYP methods approximations with 6-31G(d,p), 6-311G(d,p), and 6-311++G(d,p) basis sets allow to obtain the correct spectral pattern. A linear correlations between the calculated and experimental values of the ^{13}C chemical shifts for the studied hydroperoxide molecule were obtained for all solvents studied. In all cases, the MP method combined with 6-31G(d,p) basis set allows to get a better agreement between the calculated and experimental data as compared to the B3LYP results.

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МОЛЕКУЛЯРНОЕ МОДЕЛИРОВАНИЕ NMR ^{13}C СПЕКТРА 1,1,3-ТРИМЕТИЛ-3-(4-МЕТИЛФЕНИЛ)БУТИЛ ГИДРОПЕРЕКИСИ В РАЗЛИЧНЫХ РАСТВОРИТЕЛЯХ

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Аннотация. В работе был проведен GIAO-расчет NMR ^{13}C химических сдвигов, полученных на различных вычислительных уровнях гидроперекиси 1,1,3-триметил-3-(4-метилфенил)бутил. Данные сопоставлены с экспериментальными данными, ориентируясь на согласованность спектральной структуры и спектральных трендов. Сравнительный анализ экспериментальных и компьютерных результатов показал, что метод GIAO может использоваться для оценки химических сдвигов.

Ключевые слова: NMR-спектроскопия, 1,1,3-триметил-3-(4-метилфенил)бутил гидроперекись, химический сдвиг, постоянная магнитного экранирования, GIAO, молекулярное моделирование.