Introduction Quantum chemical methods are widely used for investigation the structural features of the organic peroxides and their associates with various classes of compounds, and to study the reactivity of hydroperoxides [1-4]. Computational chemistry is effective tool to get more structural information about peroxide bond activation by enzymes [5], transition metals compounds [6], amines and sulphide [3, 7], quaternary ammonium salts [1, 8]. The existing semi-empirical, ab initio and DFT - methods can reproduce the peroxides molecular geometry with sufficient accuracy [9]. Molecular modeling of the peroxide bond homolytic decomposition and hydroperoxides association processes is an additional information source of the structural effects that accompany these reactions. One of the criteria for the quantum-chemical method selection to study the hydroperoxides reactivity can be NMR 1H and 13C spectra parameters reproduction with sufficient accuracy. It should be noted that the parameters of the NMR spectra are very sensitive to slight changes in spatial and electronic structure of the molecule. The joint use of experimental and computational methods can be an information source of the structural features of the molecule caused by intra- and intermolecular interactions [10]. Calculations within the density functional theory (DFT) and perturbation theory (MP2) in the GIAO (Gauge Including Atomic Orbital) approximation for NMR spectra modeling of organic compounds are most often used, since they provided a good relationship between the computational cost and accuracy [10, 11]. The aim of this work is a substantiation of the method and basis for quantum-chemical calculation of the tert-butyl hydroperoxide NMR 1H and 13C spectra. Experimental Tert-butyl hydroperoxide ((CH3)2C-O-OH) was purified according to Ref. [12], its purity (99 %) was controlled by iodometry method. Experimental NMR 1H and 13C spectra of the hydroperoxide solutions were obtained by using the Bruker Avance II 400 spectrometer (NMR 1H - 400 MHz, NMR 13C - 100 MHz) at 298 K. Solvents - acetonitrile-d3 (CD3CN), chloroform-d (CDCl3), and dimethyl sulfoxide-d6 (DMSO-d6) were Sigma-Aldrich reagents and used without additional purification but were stored above molecular sieves before using. Tetramethylsilane (TMS) was used as internal standard. The hydroperoxide concentration in solution was 0.03 mol•dm-3. Molecular geometry and electronic structure parameters, thermodynamic characteristics of the tert-butyl hydroperoxide molecule were calculated using the GAUSSIAN03 [13] software package. The hydroperoxide molecular geometry optimization and frequency harmonic vibrations calculation were carried out on the first step of investigations. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same theory level. To choose the optimal method for the (CH3)2C-O-OH geometry calculation the hydroperoxide structure parameters were estimated by Hartree-Fock (HF), DFT (B3LYP and BHandHLYP) methods as well as on the MP2 theory level. The following basis sets were used in calculations: 6-31G, 6-31G(d), and 6-31G(d,p). The solvent effect was considered in the PCM approximation [14, 15]. The magnetic shielding tensors (c, ppm) for 1H and 13C nuclei of the hydroperoxide molecule were calculated with the MP2/6-

31G(d,p) and MP2/6-31G(d,p)/PCM optimized geometries by standard GIAO (Gauge-Independent Atomic Orbital) approach [16]. Optimization of the molecular geometry in the same approximation and calculation of magnetic shielding tensors in the framework of the GIAO approach were also performed for the TMS molecule. Obtained c values for TMS (Table 1) were used for the hydroperoxide 1H and 13C nuclei chemical shifts calculations. Table 1 - The magnetic shielding tensors for 1H and 13C nuclei of the tetramethylsilane molecule calculated within GIAO/MP2/6-31G(d,p) approach Solvent χH, ppm χC, ppm - 31.958 207.541 CH3CN 31.952 207.925 CHCl3 31.945 207.815 DMSO 31.940 207.858 Note: (χ vales are averaged over corresponding nuclei) Inspecting the overall agreement between experimental and theoretical spectra RMS errors (s) were used to consider the quality of the 1H and 13C nuclei chemical shifts calculations. Results and discussions Experimental NMR 1H and 13C spectra of tert-butyl hydroperoxide Experimental NMR 1H and 13C studies of tert-butyl hydroperoxide were carried out in the following solvents: acetonitrile-d3, chloroform-d and dimethyl sulfoxide-d6 at 298 K. The concentration of the hydroperoxide in all samples was 0.03 mol·dm-3. Tetramethylsilane was used as the internal standard. Parameters of the experimental NMR 1H and 13C spectra of the (CH3)3C-O-OH are listed in Table 2. Table 2 - Experimental parameters of the tert-butyl hydroperoxide NMR 1H and 13C spectra Solvent ε [17] δ (1H), ppm. δ (13C), ppm -CH3 -COOH -CH3 -COOH CDCl3 4.8 1.27 7.24 25.71 80.87 CD3CN 37.5 1.18 8.80 26.27 80.53 DMSO-d6 46.7 1.12 10.73 26.01 76.56 Table 2 reveals the following features. The shift of the -CH3 and-COOH groups signals in the NMR 1H spectrum of the hydroperoxide with the solvent polarity increasing is observed. The signal of the hydroperoxide group proton appears at 7.24 ppm in chloroform-d, and in the more polar dimethyl sulfoxide-d6 it was found at 10.73 ppm. When passing from CDCl3 to DMSO-d6 the signal of the -CH3 groups protons are shifted to the strong field. Another effect is observed in the case of the NMR 13C spectrum, the signal of a tertiary carbon atom is shifted to a strong field on 4.34 ppm in DMSO-d6 as compared to CDCl3. Equilibrium configuration of the tert-butyl hydroperoxide in the HF, MP2, and DFT methods approximation The first step of the (CH3)3C-O-OH NMR spectra calculatuion was the estimation of the hydroperoxide molecular geometry parameters and electronic structure to choose method and basis set for the further investigations. The (CH3)3C-O-OH molecular geometry optimization was carried out by HF, DFT (B3LYP и BHandHLYP) and MP2 methods, the following basis sets were used in calculations: 6-31G, 6-31G(d), and 6-31G(d,p). 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. Table 3 illustrates the influence of theory level as well as basis set on the -CO-OH fragment geometry parameters. The calculation results were compared with experimental values [18]. The best agreement between calculated and experimental parameters can be seen in the case of MP2/6-31G(d,p) method. Thus it was used in the further calculations. Table 3 - Molecular geometry parameters of -COOH moiety of the tert-butyl hydroperoxide molecule

Method/ basis set Bond length, Å Angle, ° C-O O-O O-H COO OOH COOH HF/6-31G 1.464 1.459 0.954 108.8 101.2 166.9 HF/6-31G (d) 1.426 1.393 0.948 110.3 101.9 117.6 HF/6-31G (d,p) 1.426 1.394 0.945 110.2 102.3 115.9 B3LYP/ 6-31G 1.489 1.529 0.984 107.7 98.4 134.4 B3LYP/ 6-31G(d) 1.450 1.457 0.973 109.2 99.7 110.9 B3LYP/ 6-31G(d,p) 1.450 1.458 0.971 109.1 99.8 110.7 BHandHLYP/6-31G 1.468 1.487 0.968 107.8 99.8 144.7 BHandHLYP/6-31G(d) 1.431 1.419 0.960 109.4 100.9 113.4 BHandHLYP/6-31G(d,p) 1.432 1.419 0.957 109.3 101.0 113.4 MP2/6-31G 1.501 1.575 0.988 106.3 95.5 152.5 MP2/6- 31G(d) 1.448 1.472 0.977 108.0 98.2 116.8 MP2/6-31G(d,p) 1.446 1.473 0.970 107.7 98.2 114.7 Experiment [18] 1.443 1.473 0.990 109.6 100.0 114.0 Calculations with solvent effect accounting were al so carried out for the (CH3)3C-O-OH molecule by MP2/6-31G(d,p) method within PCM approximation. Obtained geometry parameters are listed in Table 4. The solvent does not affect the O-O bond length. Solvent effect is noticeable for O-H and C-O bonds, O-O-H and C-O-O bond angles, and C-O-O-H torsion angle. Significant changes of O-H and C-O bonds, O-O-H and C-O-O bond angles are observed in the case of CH3CN and DMSO, while CHCl3 has less influence. Table 4 - Molecular geometry parameters of the tert-butyl hydroperoxide molecule calculated within MP2/6-31G(d,p)/PCM approximation Parameter Solvent - CH3CN CHCl3 DMSO rO-O,Å 1.473 1.472 1.472 1.472 rO-H,Å 0.970 0.986 0.980 0.986 rC-O,Å 1.446 1.450 1.449 1.450 ĐO-O-H,° 98.2 99.4 98.9 99.3 ĐC-O-O, ° 107.7 108.2 107.9 108.1 ĐC-O-O-H, ° 114.7 113.7 116.3 114.5 Thus MP2/6-31G(d,p) and PCM/MP2/6-31G(d,p) equilibrium configuration of the tert-butyl hydroperoxide will be used for the further calculations. GIAO NMR 1H and 13C spectra of the tert-butyl hydroperoxide With regard to the results obtained from this foregoing study, the GIAO calculations for the tert-butyl hydroperoxide molecule were performed at MP2/6-31G(d,p) level of theory in the approximation of the isolated molecule as well as with solvent effect accounting within PCM approach. Fig. 1 illustrates the structural model of the tert-butyl hydroperoxide molecule (equilibrium configuration obtained at MP2/6-31G(d,p) level of theory) with atom numbering used for GIAO NMR 1H and 13C spectra parameters representation. 1 2 3 5 10 12 6 14 13 15 4 7 8 9 16 11 Fig. 1 - Tert-butyl hydroperoxide structural model with corresponding atom numbering (MP2/6-31G(d,p)) To estimate the hydroperoxide NMR 1H and 13C spectra parameters the magnetic shielding constants (c, ppm) for corresponding nuclei were calculated by GIAO method. Obtained c values for magnetically equivalent nuclei were averaged and listed in Table 5. On the base of the obtained c values the chemical shift values (d, ppm) of the 1H and 13C nuclei in the hydroperoxide molecule were evaluated. TMS was used as standard, for which the molecular geometry optimization and c calculation were performed using the same level of theory and basis set. Values of the 1H and 13C chemical shifts were found as the difference of the magnetic shielding tensors of the corresponding TMS and hydroperoxide nuclei. For the MP2/6-31G(d,p) calculated 1H and 13C chemical shifts there was no full conformity with the experimental data. Experimental d values for -CO-OH moiety proton in all solvents are higher than the d =

6.805 ppm calculated in the isolated molecule approximation. The labile protons signals are usually shifted to lower field in DMSO-d6 solution. Difference between d values of -CO-OH moiety proton for CH3CN and CHCl3 solutions may also be due to the influence of the solvent. Formation of hydroperoxides self-associates are possible in the low-polarity solvents [19] that may affect the magnitude of the proton chemical shift of the -CO-OH fragment. Fig. 2 presents one of many possible configurations of the tert-butyl hydroperoxide molecule dimer. Molecular geometry optimization of this homoassociate was performed at MP2/6-31G(d,p) theory level without solvent effect accounting. This associate is stabilized by the formation of two intermolecular hydrogen bonds: O…HO distance is 1.834 Å, bond angle O…H-O - 161.51°, O-H bond length increases up to 0.982 Å. However, the configuration of the hydroperoxide fragment is not largely changed. For this associate c values were calculated of by GIAO method (MP2/6-31G(d,p) theory level, isolated molecule approximation) and the chemical shift values of the 1H and 13C nuclei were evaluated. The d value of 10.541 ppm has been obtained for the -CO-OH moiety proton. This is significantly higher than the experimental values observed in chloroform-d and acetonitrile-d3 solutions. Fig. 2 - Structural model of the tert-butyl hydroperoxide dimer (MP2/6-31G(d,p)) Study the hydroperoxide concentration effect on the signals position in the NMR 1H spectrum in CD3CN and CDCl3 solutions has been carried out. The hydroperoxide concentration was ranged within (2.1•- 500.0)•10-3 и (9.0 - 20.0)•10-3 mol·dm-3 in CD3CN and CDCl3 respectively. Changing in the hydroperoxide concentration in these ranges does not lead to a change in the signal position in the spectrum. Hence, the chemical shift of the hydroperoxide group proton is independent of the hydroperoxide concentration in the system in experimental conditions. Thus, calculation and NMR 1H spectroscopy results showed that the hydroperoxide dimers do not formed in the system. And observed chemical shift values for the -CO-OH moiety proton are due to the solvent effect. In order to account for the solvent effect in the calculation of magnetic shielding tensors the PCM approach was used. Magnetic shielding tensors for 1H and 13C nuclei of the tert-butyl hydroperoxide, calculated by GIAO method at MP2/6-31G(d,p) theory level with PCM solvent effect (Tables 5 and 6) have been used for the chemical shift values of the 1H and 13C nuclei estimation. Table 6 illustrates the chemical shift values (d, ppm) for 1H and 13C nuclei of the tert-butyl hydroperoxide, calculated at MP2/6-31G(d,p) level of theory with solvent effect accounting. Table 5 - GIAO-magnetic shielding tensors for 1H and 13C nuclei of the tert-butyl hydroperoxide, calculated at MP2/6-31G(d,p) theory level Sol vent NMR 1H NMR 13C -COOH -CH3 -COOH -CH3 χ, ppm d, ppm χ, ppm d, ppm χ, ppm d, ppm χ, ppm d, ppm - 25.15 6.805 30.73 1.226 128.16 79.379 180.38 27.163 CH3CN 23.18 8.771 30.70 1.250 127.61 80.311 180.47 27.455 CHCl3 23.82 8.136 30.71 1.243 127.84 79.977 180.42 27.394 DMSO 23.16 8.778 30.70 1.238 127.64 80.219 180.47 27.391 Table 6 - GIAO chemical shifts of the 1H and 13C nuclei of the tert-butyl hydroperoxide (MP2/6-31G(d,p)/PCM) Atom CH3CN CHCl3 1 2 Δ 1 2 Δ d, ppm NMR 13C C3 80.31 80.53 0.22 79.98 80.87 0.89 C4 27.94

26.27 1.67 27.90 25.71 2.19 C5 27.11 26.27 0.84 27.21 25.71 1.50 C6 27.30 26.27 1.03 27.00 25.71 1.29 σ 1.15 2.38 d, ppm NMR 1H H7 1.06 1.18 0.12 1.04 1.27 0.23 H8 1.08 1.18 0.10 1.10 1.27 0.17 H9 1.17 1.18 0.01 1.10 1.27 0.17 H10 1.00 1.18 0.18 0.96 1.27 0.31 H11 1.09 1.18 0.09 1.06 1.27 0.21 H12 1.93 1.18 0.75 1.93 1.27 0.66 H13 1.07 1.18 0.11 1.10 1.27 0.17 H14 1.95 1.18 0.77 1.90 1.27 0.63 H15 0.93 1.18 0.25 0.89 1.27 0.38 H16 8.78 8.80 0.02 8.13 7.24 0.89 σ 0.13 0.20 Atom DMSO 1 2 Δ d, ppm NMR 13C C3 80.22 76.56 3.66 C4 27.88 26.01 1.88 C5 27.07 26.01 1.06 C6 27.22 26.01 1.21 σ 4.88 d, ppm NMR 1H H7 1.05 1.12 0.07 H8 1.07 1.12 0.05 H9 1.14 1.12 0.02 H10 0.98 1.12 0.14 H11 1.07 1.12 0.05 H12 1.92 1.12 0.80 H13 1.05 1.12 0.07 H14 1.93 1.12 0.81 H15 0.91 1.12 0.21 H16 8.77 10.73 1.96 σ 0.52 Notes: 1 - calculated, 2 - experimental; Δ - difference between the experimental and calculated hydroperoxide chemical shifts; σ - RMS errors. Concerning the spectral patterns of a -CH3 group protons, inspection of Tables 5 and 6 reveals the following features: the pattern of NMR 1H spectra of (CH3)3C-O-OH is rather correctly reproduced at selected computational level for all solvents; the best agreement between the experimental and calculated 1H and 13C chemical shifts of the -CO-OH moiety is observed for acetonitrile-d solution; for all cases solvent effect accounting leads to a better result compared to the isolated molecule approximation; calculated and experimental values of δ for -CO-OH group proton decrease symbatically with the solvent polarity increasing. But in DMSO-d6 solution a significant shift to lower field region is observed for -CO-OH group proton as compared with other solvents. Calculated δ value for this proton in DMSO is very close to the experimentally observed one in acetonitrile-d3 solution. This shift can be explained by the formation of hydroperoxide-DMSO-d6 heteroassociates in experimental conditions. One should note that similar values of δ = 10.77 ¸ 10.33 ppm has a -CO-OH group proton of tert-butyl hydroperoxide complex-bonded with tetraalkylammonium bromides [20]. Conclusions The influence of the solvent on the NMR spectra parameters the of tert-butyl hydroperoxide was investigated. It is shown that with increasing polarity of the solvent signal of the hydroperoxide group proton shifts toward weak fields. On the basis of the complex data analysis of the spectroscopic studies and molecular modeling shows that the GIAO method with the MP2/6-31G (d,p) level of theory and the PCM approximation can be used to estimate NMR 1H and 13C spectra parameters of tert-butyl hydroperoxide.