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Synthesis, characterization and DFT studies of hydrazones of cycloalkanespirodithiohydantoins

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This article presents a method for synthesis of hydrazones of cycloalkanespirodithiohydantoins. The initial spirodithiohydantoins were prepared by an interaction of cycloalkanespiro-5-hydantoins with P_4S_{10} and hexamethyldisiloxane. This method yielded products with a higher yield, compared to the known methods in the literature. The spirodithiohydantoins obtained were subjected to an interaction with hydrazine hydrate. As a result 4-hydrazones of the corresponding spirodithiohydantoins were obtained. The structures of all obtained products were verified *via* ^{1}H, ^{13}C NMR and IR spectroscopy. The structures of 4-hydrazinylidene-1,3-diazaspiro[4.4]nonane-2-thione, 4-hydrazinylidene-1,3-diazaspiro[4.5]decane-2-thione, 4-hydrazinylidene-1,3-diazaspiro[4.6]undecane-2-thione and 4-hydrazinylidene-1,3-diazaspiro[4.7]dodecane-2-thione were optimized using Density Functional Theory (DFT) methods at B3LYP/6-31G(d,p) level. The theoretical IR and NMR spectra of the compounds were calculated at B3LYP/6-31G(d,p) and B3LYP/6-31+G(2d,p) levels, respectively and were compared to experimental data. A good agreement between the DFT predicted and the experimentally measured IR and NMR spectra of the hydrazones was found.

Key words: Hydrazones, cycloalkanespiro-5-(2,4-dithiohydantoins), DFT

INTRODUCTION

In a previous work we reported two methods for cycloalkanespiro-5-hydantoins thionation [1]. These methods were based on the reaction of the respective spirohydantoins (with five-, six-, seven-, eight- and twelve-membered cycloalkane substituent at 5th position in the hydantoin ring) with Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, LR) or P_4S_{10}. Thionation of spirohydantoins with LR as cited above was performed in toluene medium under refluxing for six hours. This procedure led to obtaining of products with high yields (82 – 96 %). On the other hand, the use of P_4S_{10} as a thionation reagent (refluxing for five hours in xylene medium) resulted in formation of spirodithiohydantoins with 7 – 28 % lower yields of products as compared to those obtained through the method previously commented [1]. Recently, we reported a method for synthesis of cyclopentanespiro-5-(2,4-dithiohydantoin), based on the interaction of cyclopentanespiro-5-hydantoin with a combination of P_4S_{10} and hexamethyldisiloxane (HMDO), following a modification of a procedure developed by Curphey [2]. This technique led to a significant reduction of the reaction time (1.5 hours) and to obtaining a product of higher yield (92 %), compared to the thionation methods mentioned above [1]. It was also found out that this compound showed an *in vitro* insecticidal activity against *Cladius pectinicornis* [3], Mealy plum aphid (*Hyalopterus pruni*) [4] and Oleander aphid (*Aphis nerii*) [5], as well as an *in vitro* fungicidal activity towards *Blumeria graminis* f. sp. *tritici* [6]. This work is a continuation of our previous studies for the development of more effective spirohydantoins thionation techniques. The current study presents the thionation of a series of cycloalkanespiro-5-hydantoins with a combination of P_4S_{10} and HMDO, as well as the interaction of the dithio analogues obtained with hydrazine hydrate, resulting in formation of the corresponding 4-hydrazones.

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EXPERIMENTAL

General

All chemicals used were purchased from Merck and Sigma-Aldrich. The melting points were determined with a digital melting point apparatus SMP 10. The elemental analysis data were obtained with an automatic analyzer Carlo Erba 1106. The purity of the compounds was checked by thin layer chromatography on Kieselgel 60 F_{254}, 0.2 mm Merck plates, eluent systems (vol. ratio): (a) chloroform : acetone = 9 : 1, (b) ethylacetate : petroleum ether = 1 : 5. IR spectra were taken on spectrometers Bruker-113 and Perkin-Elmer FTIR-1600 in KBr discs. NMR spectra were taken on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^{1}H and ^{13}C, respectively, using the standard Bruker software. Chemical shifts were referenced to tetramethylsilane (TMS). Measurements in DMSO-d_6 solutions were carried out at ambient temperature (300 K). The initial cycloalkanespiro-5-hydantoins 1a-4a (Scheme 1) were synthesized *via* the Bucherer-Lieb method [7]. The compounds 1a-4a were thionated with the combination of P_4S_{10} and hexamethyldisiloxane (HMDO), following a modification of a procedure developed by Curphey [2] (Scheme 1).

Synthesis of cycloalkanespirodithiohydantoins 1b-4b (a modification of the method reported by Curphey [2]) (Scheme 1)

A mixture of 0.03 mol of the corresponding cycloalkanespiro5-hydantoin (1a-4a), 4.89 g (0.011 mol) of P_4S_{10}, 21 ml (0.1 mol) of hexamethyldisiloxane (HMDO) and 60 ml of xylene was refluxed for an hour and a half. After cooling, the obtained crystalline product (1b-4b) was filtered off and recrystallized from methanol/water solution. The physicochemical parameters and the IR and NMR spectral data of the compounds were identical with the previously published data [1, 3].

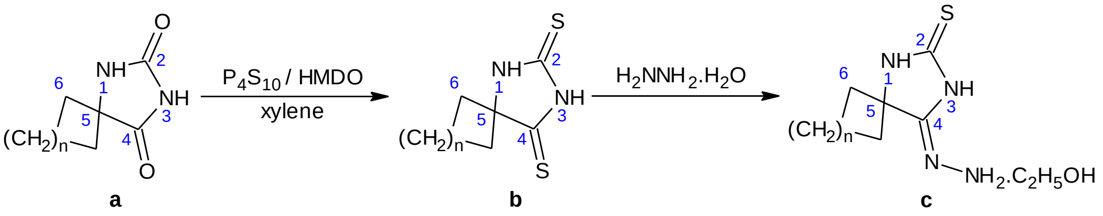
Synthesis of 4-hydrazones of cycloalkanespirodithiohydantoins 1c-4c (Scheme 1)

5.15 g (0.1 mol) of 95 % hydrazine hydrate was added to 0.004 mol of the corresponding cycloalkanespiro-5-(2,4-dithiohydantoin) (1b-4b) at room temperature. A small quantity of crushed ice was added to the reaction mixture. The crystalline product (1c-4c) obtained was filtered off and recrystallized from ethanol. The physicochemical parameters and the IR and NMR spectral data of the compounds (including an ethanol molecule in their structure) are listed in Tables 1 and 2, respectively.

COMPUTATIONAL DETAILS

The optimized geometries of the compounds 1c-4c (Fig. 2) were located by Density Functional Theory (DFT) using GAMESS (US) quantum chemistry package [8]. Geometry optimization of these structures was carried out by the hybrid B3LYP functional which combines the three-parameter exchange functional of Becke [9] with the LYP correlation one [10] using 6-31G(d) basis set. The calculations were carried out without symmetry constraints by the gradient procedure. A gradient convergence threshold of 1×10^{-4} hartree Bohr^{-1} was used.

The proton and carbon chemical shieldings were calculated with the B3LYP functional and 6-31+G(2d,p) basis set using the gauge-including atomic orbitals (GIAO) approach [11, 12] and B3LYP/6-31G(d) optimized geometry. The including of the solvent as dielectric (polarizable continuum model) in GIAO NMR calculations was used to estimate the effect of the medium (DMSO) on the chemical shifts of 1c-4c compounds. In order to compare with the experimental data, the calculated absolute shieldings were transformed to chemical shifts using the reference compound tetramethylsilane (TMS): $\delta = \delta_{calc}(\text{TMS}) - \delta_{calc}$. Both $\delta_{calc}(\text{TMS})$ and δ_{calc} were evaluated with the same method and basis set. The NMR calculations were carried out using GAUSSIAN 09 program package [13].



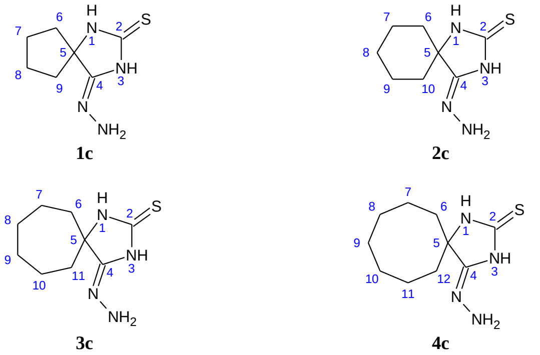
1-4 n = 2-5

Scheme 1. Synthesis of 4-hydrazinylidene-1,3-diazaspiro[4.4]nonane-2-thione (1c), 4-hydrazinylidene-1,3-diazaspiro[4.5]decane-2-thione (**2c**), 4-hydrazinylidene-1,3-diazaspiro[4.6]undecane-2-thione (**3c**) and 4-hydrazinylidene-1,3-diazaspiro[4.7]dodecane-2-thione (**4c**)

RESULTS AND DISSCUSION

The synthesis of the compounds was performed in accordance with Scheme 1. The cycloalkanespiro-5-hydantoins 1a-4a were synthesized by the Bucherer-Lieb method [7], based on the interaction between the corresponding ketone, sodium or potassium cyanide, ammonium carbonate and ethanol. The compounds obtained (1a-4a) were subjected to thionation with the combination of P_4S_{10} and hexamethyldisiloxane (HMDO), following a modification of the procedure developed by Curphey [2]. The advantage of this method is the significant reduction of the reaction time (from 5 or 6 hours to 1.5 hours), and obtaining products of higher yield compared to previously used thionation methods [1]. Yields of the spirodithiohydantoins obtained were as follows: 1b - 92 % [3]; 2b - 96 %; 3b - 99 %; 4b - 98 %. The physicochemical parameters and the IR and NMR spectral data of the compounds 1b-4b were identical with the previously published data [1, 3].

The compounds 1b-4b were subjected to an interaction with hydrazine hydrate. The literature data available showed that the refluxing of cycloalkanespiro-5-hydantoins with hydrazine hydrate led to obtaining of the relevant 3-amino derivatives [14]. Additionally, the treatment of cyclohexanespiro-5-(2-thiohydantoin) with hydrazine hydrate at different reaction conditions was studied [15]. It was found that refluxing of cyclohexanespiro-5-(2-thiohydantoin) with hydrazine hydrate resulted in formation of the relevant 3-amino derivative. On the other hand, when the reaction was done at normal conditions, the corresponding 2-hydrazone was obtained. Now, we examined the interaction of four cycloalkanespirodithiohydantoins with hydrazine hydrate (Scheme 1) at room temperature. The spectral data obtained clearly showed that in this case the substitution was realized at C^4 of the dithiohydantoin ring, and an ethanol molecule was present in the structures of the compounds 1c-4c. The spectral data obtained were in compliance with previously published results about synthesis of hydrazones of cyclododecanespiro-5-(2,4-dithiohydantoin) and spiro-(fluorene-9,4’-imidazolidine)-2’,5’-dithione [16]. The physico-chemical parameters and the IR and NMR spectral data of the compounds 1c-4c are listed in Table 1 and Table 2. The structural formulas and atom numbering of the compounds synthesized are presented in Figure 1.



1c 2c 3c 4c

Fig. 1. Structural formulas and atom numbering of the compounds synthesized.

It is well known that DFT often gives calculated magnetic shieldings in large systems of a quality comparable or even better than MP2 for a cost that is of the same order as Hartree–Fock, substantially less than that of traditional correlation techniques [17-19]. Exchange–correlation functionals are believed to be superior in predicting molecular properties [20, 21]. We carried out calculations using B3LYP and BPW91 functionals, and found the B3LYP results to be closest to experimental data. Therefore, we present only the B3LYP results in GIAO NMR calculations in DMSO. Because of the sensitivity of ^{13}C NMR chemical shifts to the presence of polarization and diffuse functions in the basis set, the 6-31+G(2d,p) basis set was employed [22, 23]. Our theoretical results are in agreement with the ^1H and ^{13}C NMR measurements in DMSO-d_6 solution of compounds 1c-4c.

The vibrational spectra of the 4-hydrazinylidene-1,3-diazaspiro[4.4]nonane-2-thione (1c), 4-hydrazinylidene-1,3-diazaspiro[4.5]decane-2-thione (2c), 4-hydrazinylidene-1,3-diazaspiro[4.6]undecane-2-thione (3c) and 4-hydrazinylidene-1,3-diazaspiro[4.7]dodecane-2-thione (4c) were computed at B3LYP/6-31G(d,p) level. Available experimental data for the vibrational frequencies of the four compounds in KBr are presented for comparison. All results are listed in Table 2. Our assignments for the DFT calculated frequencies are based upon the analysis of the corresponding vibrational eigenvectors. Some modes such as NH, C=S, C=N stretching and NH_2 deformation were found to be characteristic. The analysis of the theoretical spectra of the four compounds shows that there is a good agreement with experimental data.

On the base of the good accordance in theoretically found molecular properties we have investigated the performance of the hybrid density functional B3LYP for predicting geometrical parameters of the 1c-4c compounds. The B3LYP/6-

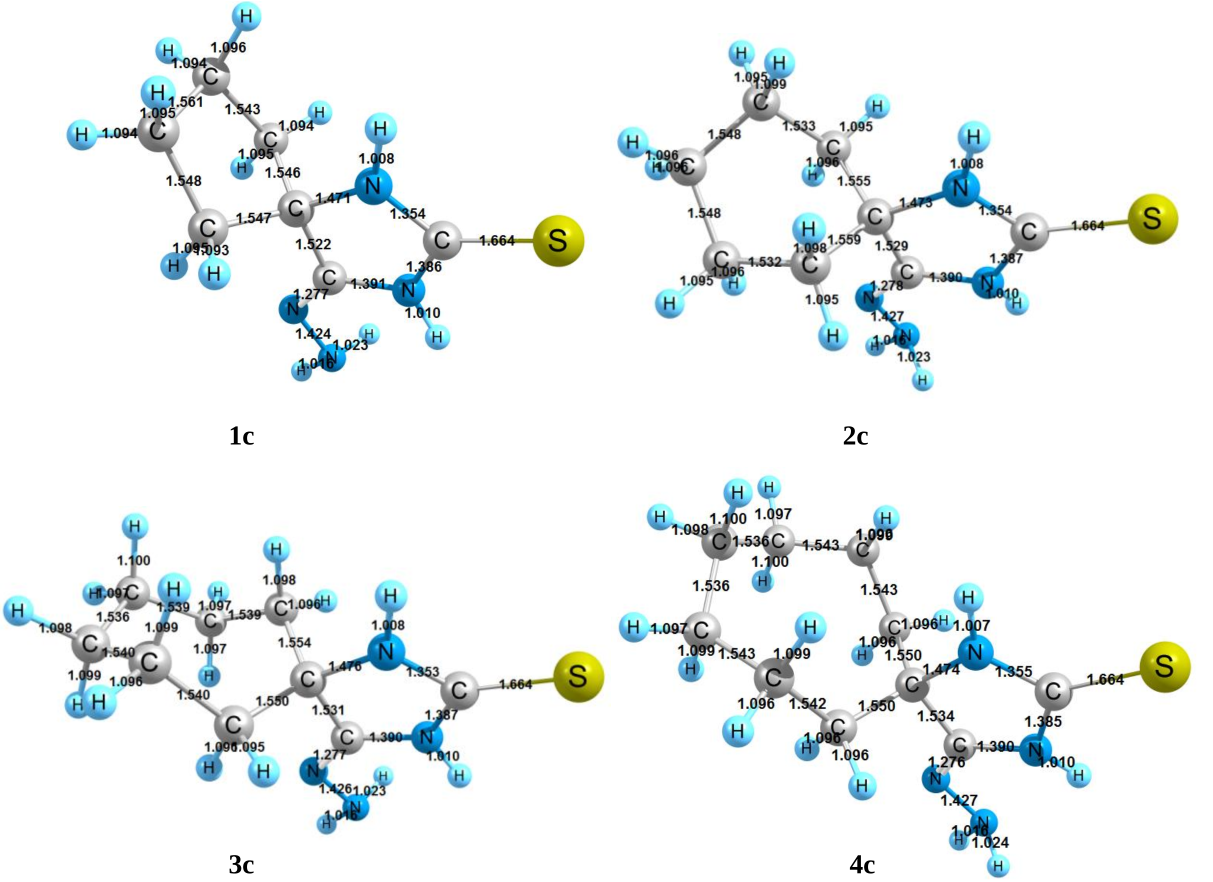
31G(d,p) optimized geometries and interatomic distances of the 1c-4c molecules are presented in Figure 2. The augmentation of the cycloalkane ring in the hydrazone molecules from 4-hydrazinylidene-1,3-diazaspiro[4.4]nonane-2-thione (1c) to 4-hydrazinylidene-1,3-diazaspiro[4.7]dodecane-2-thione (4c) induces some changes in the geometrical parameters of the imidazolidine moiety. They are mainly related to the changes in C-C bonds. According to calculations at B3LYP/6-31G(d,p) level the C–C bond in the imidazolidine ring is lengthened from 1.522 Å in 1c to 1.534 Å in 4c. The lengthening of this bond in 2c is by 0.007 Å while in 3c and 4c it is 0.009 Å and 0.012 Å, respectively. There is little change in the C-C bonds in the cycloalkane moiety. The bonds that connect the cycloalkane ring to the imidazolidine moiety are shortest in the 1c molecule and longest in the 2c one. There is no alteration in the rest of bonds in the hydrazone molecules as a result of cycloalkane ring augmentation.

Table 1. Physico-chemical parameters and elemental analysis data of compounds 1c-4c

№ [a]	Yield, %	M.p., ˚C	R_f [b]		Anal. calcd. (found) / %			
			i	ii	C	H	N	S
1c	54	231-232	0.53	0.11	46.93 (46.87)	7.88 (7.85)	24.32 (24.13)	13.92 (13.26)
2c	55	206-207	0.63	0.19	49.15 (49.02)	8.25 (8.18)	22.93 (22.78)	13.12 (12.99)
3c	69	193-194	0.60	0.15	51.13 (51.00)	8.58 (8.49)	21.68 (21.58)	12.41 (12.07)
4c	66	265-266	0.68	0.34	52.91 (52.78)	8.88 (8.81)	20.57 (20.48)	11.77 (11.37)

[a] The compounds numbering is in accordance with Scheme 1.

[b] Eluent systems (vol. ratio): i) chloroform : acetone = 9 : 1; ii) ethylacetate : petroleum ether = 1 : 5.



1c **2c**

3c **4c**

Fig. 2. B3LYP/6-31G(d,p) optimized structures of compounds 1c–4c. The bond lengths (in Å) are also given.

Table 2. Experimental IR, ^1H and ^{13}C NMR data of compounds 1c–4c[a]. Selected IR frequencies calculated at B3LYP/6-31G(d,p) level and GIAO ^1H and ^{13}C chemical shifts calculated (in italic) at B3LYP/6-31+G(2d,p) level. The frequencies are scaled by 0.945

№	IR (KBr) ν_{max} / cm^{-1}	^{1}H NMR (DMSO-d$_6$) δ / ppm	^{13}C NMR (DMSO-d$_6$) δ / ppm ^{b}
1c	3289, 3256, 3178 *3480, 3457, 3372, 3234* (NH, NH$_2$); 2972-2889 *2957- 2886* (CH$_2$); 1697 *1673* (C=N); 1519, 1161 *1454, 1185* (C=S)	1.00-1.05 (m, 3H, CH$_3$/EtOH), 1.67-1.91 *1.87-2.08* (m, 8H, CH$_2$), 5.24 (s, 1H, OH/EtOH), 9.58 *8.63* (s, 2H, NH$_2$), 10.49 (s, 1H, N^3-H)	18.8 (CH$_3$/EtOH), 23.8 *26.8* (C^7, C^8), 39.5 *43.1* (C^6, C^9), 56.2 (CH$_2$/EtOH), 70.3 *77.4* (C^5), 178.1 *177.1* (C^2), 145.9 *152.6* (C^4)
2c	3432, 3347, 3319, 3198 *3476, 3453, 3371, 3236* (NH, NH$_2$), 2939-2792 *2937-2859* (CH$_2$), 1703 *1670* (C=N), 1542, 1093 *1455, 1092* (C=S)	1.00-1.06 (m, 3H, CH$_3$/EtOH), 1.42-1.73 *1.50-2.07* (m, 10H, CH$_2$), 5.25 (s, 1H, OH/EtOH), 9.72 *8.57* (s, 2H, NH$_2$), 10.52 (s, 1H, N^3-H)	18.6 (CH$_3$/EtOH), 20.8 *21.3* (C^7, C^9), 24.7 *24.3* (C^8), 36.2 *36.6* (C^6, C^{10}), 56.1 (CH$_2$/EtOH), 64.0 *68.6* (C^5), 178.7 *177.0* (C^2), 145.7 *156.8* (C^4)
3c	3348, 3223, 3155 *3476, 3453, 3372, 3235* (NH, NH$_2$), 2931-2848 *2928, 2846* (CH$_2$), 1703 *1670* (C=N), 1532, 1090 *1452, 1113* (C=S)	1.00-1.06 (m, 3H, CH$_3$/EtOH), 1.22-1.99 *1.32-2.02* (m, 12H, CH$_2$), 5.26 (s, 1H, OH/EtOH), 9.90 *8.50* (s, 2H, NH$_2$), 11.01(s, 1H, N^3-H)	18.8 (CH$_3$/EtOH), 21.5 *26.9* (C^7, C^{10}), 29.6 (C^8, C^9), 39.6 *43.4* (C^6, C^{11}), 56.4 (CH$_2$/EtOH), 66.8 *72.4* (C^5), 178.2 *176.8* (C^2), 147.1 *156.2* (C^4)
4c	3329, 3208, 3163 *3490, 3457, 3370,3232,* (NH, NH$_2$); 2919-2847 *2922-2843* (CH$_2$); 1689 *1673* (C=N); 1538, 1194 *1450, 1125* (C=S)	1.00-1.05 (m, 3H, CH$_3$/EtOH), 1.45-1.67 *1.25-2.12* (m, 14H, CH$_2$), 5.10 (s, 1H, OH/EtOH), 9.64 *8.44* (s, 2H, NH$_2$), 10.30 (s, 1H, N^3-H)	18.6 (CH$_3$/EtOH), 20.8 *28.0* (C^7, C^{11}), 24.1 (C^9), 27,7 (C^8, C^{10}), 34.1 (C^6, C^{12}), 56.1 (CH$_2$/EtOH), 66.6 *71.3* (C^5), 178.5 *177.8* (C^2), 148.0 (C^4)

[a] Atom numbering is in accordance with Figure 1.

[b] These assignments are confirmed by the DEPT-135 spectral data.

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СИНТЕЗ, ОХАРАКТЕРИЗИРАНЕ И КВАНТОВО-ХИМИЧНИ ИЗЧИСЛЕНИЯ С ПОМОЩТА НА ТЕОРИЯТА НА ФУНКЦИОНАЛА НА ПЛЪТНОСТТА НА ХИДРАЗОНИ НА ЦИКЛОАЛКАНСПИРОДИТИОХИДАНТОИНИ

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(Резюме)

Статията представя метод за синтез на хидразони на циклоалканспиродитиохидантоини. Изходните спиродитиохидантоини бяха получени при взаимодействие на циклоалканспиро-5-хидантоини с P_4S_{10} и хексаметилдисилоксан. Този метод води до синтез на продукти с по-висок добив, в сравнение с известни литературни данни. Спиродитиохидантоините бяха подложени на взаимодействие с хидразин хидрат, в резултат на което бяха получени съответните 4-хидразони. Структурата на продуктите беше потвърдена чрез ^{1}H, ^{13}C ЯМР и ИЧ спектроскопия.

Структурите на 4-хидразинилиден-1,3-диазаспиро[4.4]нонан-2-тион, 4-хидразинилиден-1,3-диазаспиро[4.5] декан-2-тион, 4-хидразинилиден-1,3-диазаспиро[4.6]ундекан-2-тион и 4-хидразинилиден-1,3-диазаспиро[4.6] додекан-2-тион бяха оптимизирани с помощта на теорията на функционала на плътността на ниво B3LYP/6-31G(d,p). Със същия функционал бяха изчислени теоретичните ИЧ и ЯМР (протонни и въглеродни) спектри на съединенията, като за предсказване на ^{1}H и ^{13}C ЯМР спектри беше използван 6-31+G(2d,p) базисен набор, а за предсказване на ИЧ спектрите - 6-31G(d,p) базисен набор. Намерено беше добро съответствие между теоретичните и експерименталните резултати.