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Multinuclear magnetic resonance studies of 2-aryl-1,3,4-thiadiazoles

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The ^{1}H, ^{13}C and ^{15}N spectra of aryl-substituted 1,3,4-thiadiazoles were recorded. The results obtained were correlated with Hammett coefficients. The experimental results were compared with DFT-calculated chemical shifts. The results obtained were compared with those for 1,3,4-oxadiazoles and 1,3,4-selenadiazoles. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

1,3,4-Thiadiazoles make an interesting group of heterocyclic molecules. The compounds containing 1,3,4-thiadiazole moiety show interesting pharmacological activities as well as properties useful from the technological and agricultural point of view.[1–5] Their antibacterial,[6–11] antiviral,[12–15] anticancer,[11,13,16] antiparasitic,[17–19] anti-inflammatory,[14] anticholinergic[7] and antihistamine[7,20] activities have been widely studied. Some compounds belonging to this class are potent radioprotective agents.[21,22] 1,3,4-Thiadiazoles were also used as lubricants,[23–26] dyes,[27–29] corrosion and oxidation inhibitors,[24,30–33] liquid crystals[34,35] and optoelectronic materials.[36–38] Moreover, their herbicidal,[39] insecticidal,[40–42] fungicidal[10,43,44] and algicidal[45] properties have been investigated. Besides the information on the wide range of thiadiazoles applications and extensive studies on their chemistry, no systematic studies on their NMR properties have been published.

In our previous papers, we have presented ^{1}H, ^{13}C, ^{15}N, ^{17}O and ^{77}Se NMR studies of substituted 1,3,4-oxa(selena)diazoles.[46–49] This paper is a concise report on the NMR properties of their thia analogs.

Experimental

Synthesis

The compounds studied were prepared from the corresponding *N*-aryloyl-*N*′-formylhydrazides using Lawesson's reagent as thionation agent, according to the procedure described previously.[50] The structures of the compounds studied are presented in Fig. 1.

NMR measurements

All spectra, except ^{19}F NMR, were recorded at 298 ± 0.1 K on a Bruker Avance DRX 600 spectrometer (Billerica, MA, USA), equipped with a 5 mm triple-resonance inverse probehead (^{1}H/^{31}P/BB) with a self-shielded *z*-gradient coil (90° pulse width for ^{1}H, 9.0; for ^{13}C, 15; for ^{15}N, 11.3 µs; spectral frequencies: 600.3029, 150.9456 and 60.8511 MHz, respectively) or 5 mm BBO probehead (BB/^{1}H; 90° pulse width for ^{33}S, 7 µs; spectral frequency: 46.0793 MHz). The ^{19}F NMR experiments were made on a Varian VNMRS-400 spectrometer (Palo Alto, CA, USA) equipped with auto-switchable 5 mm probehead (90° pulse width for ^{19}F, 31.5 µs; spectral frequency 378.8194 MHz) at the same temperature. The ^{1}H, ^{13}C, ^{15}N and ^{19}F measurements were made for 0.02 M solutions in $CDCl_3$, the ^{33}S NMR experiments were made for 1 M solution. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using one-pulse sequence and standard acquisition parameters, whereas the ^{33}S NMR experiments were made with *aring2* sequence. The ^{15}N chemical shifts were obtained from two-dimensional ^{1}H–^{15}N gradient-selected HMBC experiments, performed using a standard pulse sequence from the Bruker pulse library. The delay for evaluation of multiple bond couplings was set to 31.25–62.5 ms, which corresponds to 4–8 Hz coupling constant values. The 2D spectra were recorded as 1024 × 512 matrix and the spectral widths for F_2 and F_1 were 6000 Hz for proton and 10 000 Hz for nitrogen. The sine-bell window function was applied and the zero filling to 2048 × 2048 matrix was used before Fourier transformation. Total number of scans in each increment of 2D spectra needed to obtain a satisfactory signal-to-noise factor was 32–128, depending on the compound structure. The ^{1}H and ^{13}C NMR spectra were referred to internal TMS, ^{19}F to internal $CFCl_3$, ^{15}N NMR spectra to external neat CH_3NO_2, whereas ^{33}S to external saturated solution of $(NH_4)_2SO_4$ in D_2O (0.00 ppm). The chemical shift measurements accuracy for ^{1}H, ^{13}C and ^{19}F was better than 0.01 ppm, whereas for ^{15}N, better than 0.05 ppm.

DFT calculations

The initial structures were pre-optimized by the PM3 semi-empirical method. The conformational search was performed by examining

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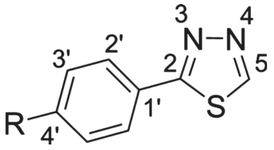

	1	2	3	4	5	6	7	8	9	10	11	12	13
R	NMe$_2$	NH$_2$	OMe	Me	CF$_3$	H	Ph	F	Cl	Br	I	CN	NO$_2$

Figure 1. The 2-aryl-1,3,4-thiadiazoles studied.

all torsion angles along exocyclic bonds using CAChe 5.0. One conformer was found to be over 16.7 kJ/mol (4 kcal/mol) more stable than other ones. The pre-optimized input structures were then fully optimized by the DFT method at the B3LYP/6-311G** (2d, 2p) level of theory with Gaussian 03.[51] The molecules were allowed to relax concurrently and without any imposed symmetry restrictions. The optimized structures were used for calculations of NMR shifts. These calculations were also performed using DFT method, at the same level of theory, which provided a good correlation with experimental results. The computed spectral and molecular parameters for iodo-substituted thiadiazole were not presented, because the iodine atom was not parameterized in this calculation basis set. The standards used for the calculations of the chemical shifts were tetramethylsilane for ^{13}C and ammonia for ^{15}N. The geometry and nuclear shielding constants of these molecules were optimized at the same level of theory as the compounds studied. The calculated shieldings are as follows: tetramethylsilane (^{13}C) 183.77 ppm and ammonia (^{15}N) 259.94 ppm. The ^{15}N chemical shifts were converted to nitromethane scale with equation: $\delta_{CH3NO2} = \delta_{NH3} - 399.3$ ppm (the value of the ^{15}N chemical shift of gaseous ammonia[52]).

Table 1. ^{1}H, ^{15}N and ^{19}F NMR parameters of the compounds studied

Compound	^{1}H, ^{15}N and ^{19}F chemical shift [ppm]					
	H-5	H-2′	H-3′	N-3	N-4	Other atoms
1	8.99	7.84	6.76	−26.89	−6.14	3.04 (NC***H***$_3$) −327.99 (***N***CH$_3$)
2	9.01	7.80	6.63	−24.51	−5.90	~ 4.1 (N***H***) −320.71 (***N***H)
3	9.07	7.91	6.97	−22.29	−5.84	3.84 (OC***H***$_3$)
4	9.10	7.87	7.27	−20.00	−5.73	2.40 (C***H***$_3$)
5	9.23	8.13	7.76	−12.29	−3.27	−63.53 (C***F***$_3$)
6	9.17	8.05	7.49	−17.96	−5.43	7.52 (*H-4′*)
7	9.08	8.01	7.65	−17.41	−5.43	7.58 (*H-2″*) 7.43 (*H-3″*) 7.36 (*H-4″*)
8	9.12	8.01	7.19	−17.43	−4.18	−108.55 (Ar-***F***)
9	9.18	7.91	7.44	−16.56	−5.27	—
10	9.16	7.85	7.61	−16.23	−4.55	—
11	9.14	7.84	7.72	−15.76	−3.99	—
12	9.27	8.15	7.67	−11.97	−3.52	−121.70 (C***N***)
13	9.30	8.20	8.36	−10.15	−4.64	−11.20 (***N***O$_2$)

Results and Discussion

The ^{1}H, ^{13}C and ^{15}N NMR experimental data were summarized in Tables 1 and 2. The calculated chemical shifts were presented in Table 3.

Table 2. ^{13}C and 33S NMR parameters of the compounds studied

Compound	^{13}C and ^{33}S chemical shift [ppm]							
	C-2	C-5	C-1′	C-2′	C-3′	C-4′	Other C atoms	S-1
1	168.77	149.64	118.70	129.35	113.32	147.62	40.33	
2	168.66	150.00	118.73	128.87	115.51	149.60	—	
3	167.83	150.47	121.99	129.42	114.32	161.73	55.21	−59
4	168.31	150.91	126.70	127.88	129.74	141.64	21.32	
5	166.69	151.94	132.75	128.32	126.10	132.71	123.48	
6	168.04	151.27	130.94	126.64	128.73	131,85	—	−55
7	167.82	151.09	128.20	126.80	128.34	143.68	139.38 (C-1″) 127.52 (C-2″) 128.75 (C-3″) 127.89 (C-4″)	
8	167.07	151.15	125.92	130.12	116.38	164.41	—	
9	166.95	151.54	127.80	129.06	129.26	137.16	—	
10	167.06	151.38	128.36	129.30	132.28	125.60	—	
11	167.36	151.35	129.03	129.42	138.35	97.84	—	
12	166.09	152.39	134.49	128.50	132.73	114.83	118.33	
13	165.97	152.77	135.10	128.96	124.45	149.19	—	

Table 3. Calculated chemical shifts

Compound	Chemical shifts [ppm]				
	C-2	C-5	C-1′	N-3	N-4
1	177.45	152.87	125.76	−6.49	19.64
2	177.09	153.29	127.58	−4.73	19.69
3	176.98	154.10	129.92	−1.30	20.22
4	177.53	154.82	134.97	2.77	20.39
5	176.36	156.51	140.57	10.86	21.63
6	177.60	155.18	137.65	5.04	21.09
7	—	—	—	—	—
8	176.22	155.32	133.62	3.79	20.96
9	176.37	155.61	135.70	5.83	21.07
10	176.41	155.64	136.44	6.26	21.23
11	—	—	—	—	—
12	176.09	156.88	140.56	12.93	22.15
13	175.75	157.53	143.44	15.64	22.89

The ^{1}H NMR parameters

The observed chemical shifts of C^5–H proton (8.99–9.30 ppm; Table 1) take values intermediate between those of 1,3,4-oxadiazoles (8.32–9.30 ppm)[49] and those of 1,3,4-selenadiazoles (9.77–10.05 ppm)[47]. The value reported for unsubstituted 1,3,4-thiadiazole (7.55 ppm)[53] is distinctly smaller than that observed for 2-aryl-substituted ones. For 1,3,4-oxa and 1,3,4-selena analogs, such differences were not observed. Moreover, for C^2–H signal of thiazole, the observed chemical shift (8.88 ppm)[53] is close to that estimated for the compounds studied here. This indicates that the result given in literature for 1,3,4-thiadiazole is incorrect and needs re-determination.

A good correlation (r^2 0.94) between the chemical shift of C^5–H proton and global Hammett constants[54] was observed. The dissection of the substituent parameter onto its resonance and inductive components indicates the equal contribution of both effects, contrary to 1,3,4-selenadiazoles for which resonance effects are predominant and 1,3,4-oxadiazoles, for which inductive effect is dominant (Table 4). This is the effect of increasing of aromaticity in the series of 1,3,4-chalcogendiazole with the increasing atomic number of chalcogen atom.

The ^{1}H NMR signals of aryl substituents show typical chemical shifts values. The value of Z_2 parameter for 1,3,4-thiadiazo-2-yl substituent, calculated from the values obtained for the studied series of compounds is 0.76 ± 0.07. This is a value intermediate between those determined for oxa and selena analogs (0.69 and 0.84, respectively). The values of $Z_3 = 0.19 \pm 0.04$ and $Z_4 = 0.26$ are the same as for 1,3,4-oxadiazo-2-yl and 1,3,4-selenadiazo-2-yl substituents.

The ^{13}C NMR parameters

Chemical shifts of both 1,3,4-thiadiazole heterocyclic ring carbon atoms are very close to that of oxadiazole analogs. The ranges of variation of the chemical shifts of these atoms are similar: 2.80 ppm for C-2 and 3.13 ppm for C-5, respectively. The values obtained for C–H of 2-aryl substituted thiadiazoles (average 151.2 ppm) are very close to this reported for unsubstituted ring (152.7 ppm).[53] The changes observed for C-2 and C-5 have

Table 4. Regression statistics for experimental data *versus* Hammett substituent parameters, calculated chemical shifts and bond lengths

Probe atom	Equation	$\rho \pm s_\rho$	$i \pm s_i$	n	r^2
C^5-**H**	$\delta_{exp}(^1H) = \rho_P \sigma_p + i$	0.19 ± 0.02	9.129 ± 0.007	13	0.939
C^5-**H**	$\delta_{exp}(^1H) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: 0.20 ± 0.02	9.14 ± 0.02	13	0.940
		ρ_I: 0.18 ± 0.04			($SD = 0.005$; $f = 0.05$)
C-2	$\delta_{exp}(^{13}C) = \rho_P \sigma_p + i$	-1.8 ± 0.2	167.54 ± 0.08	13	0.903
C-2	$\delta_{exp}(^{13}C) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: -1.2 ± 0.1	168.04 ± 0.08	13	0.982
		ρ_I: -3.0 ± 0.2			($SD = 0.12$; $f = 0.10$)
C-2	$\delta_{exp}(^{13}C) = \rho\ \delta_{calc}(^{13}C) + i$	1.4 ± 0.2	-81 ± 35	11	0.848
C-5	$\delta_{exp}(^{13}C) = \rho_P \sigma_p + i$	1.83 ± 0.08	151.12 ± 0.04	13	0.979
C-5	$\delta_{exp}(^{13}C) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: 1.9 ± 0.1	157.20 ± 0.08	13	0.981
		ρ_I: 1.6 ± 0.2			($SD = 0.12$; $f = 0.13$)
C-5	$\delta_{exp}(^{13}C) = \rho\ \delta_{calc}(^{13}C) + i$	0.66 ± 0.02	48 ± 3	11	0.992
C-1′	$\delta_{exp}(^{13}C) = \rho_P \sigma_p + i$	11 ± 1	127.0 ± 0.5	13	0.902
C-1′	$\delta_{exp}(^{13}C) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: 14 ± 1	129.6 ± 0.7	13	0.965
		ρ_I: 4 ± 2			($SD = 0.95$; $f = 0.11$)
C-1′	$\delta_{exp}(^{13}C) = \rho\ \delta_{calc}(^{13}C) + i$	1.03 ± 0.05	-12 ± 6	11	0.986
N-3	$\delta_{exp}(^{15}N) = \rho_P \sigma_p + i$	10.2 ± 0.4	-18.2 ± 0.2	13	0.985
N-3	$\delta_{exp}(^{15}N) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: 10.7 ± 0.6	-17.7 ± 0.4	13	0.987
		ρ_I: 9.2 ± 0.9			($SD = 0.53$; $f = 0.11$)
N-3	$\delta_{exp}(^{15}N) = \rho\ \delta_{calc}(^{15}N) + i$	0.75 ± 0.03	-21.3 ± 0.2	11	0.986
N-4	$\delta_{exp}(^{15}N) = \rho_P \sigma_p + i$	1.6 ± 0.4	-5.0 ± 0.1	13	0.636
N-4	$\delta_{exp}(^{15}N) = \rho_I \sigma_I + \rho_R \sigma_R + i$	ρ_R: 1.3 ± 0.6	-5.3 ± 0.4	13	0.658
		ρ_I: 2.3 ± 0.9			($SD = 0.53$; $f = 0.50$)
N-4	$\delta_{exp}(^{15}N) = \rho\ \delta_{calc}(^{15}N) + i$	0.7 ± 0.2	-20 ± 5	11	0.553

σ_p, σ_I and σ_R – global, inductive and resonance Hammett values; δ_{exp} and δ_{calc} – experimental and calculated chemical shifts of the corresponding nuclei; L – bond length; ρ – regression coefficient for the single parameter; i – intercept; s_ρ and s_i – standard deviations; n – number of compounds taken for statistical analysis; r – correlation coefficient; SD – standard deviation of regression; $f = SD/RMS$, where RMS – root mean square of SCS opposite signs, i.e. the more electron-withdrawing groups cause shielding of C-5 and deshielding of C-2 nuclei. The sensitivity of the aryl-substituted carbon atom to the electronic properties of the substituent is higher than that observed for 1,3,4-oxadiazoles (2.39 ppm), but slightly smaller than that for 1,3,4-selenadiazoles (2.84 ppm). The C-5 carbon atom of the compounds studied shows a narrower chemical shift range than the analogous atom of selenadiazoles (3.95 ppm), but it is more sensitive to the substituent character than in oxadiazoles (1.89 ppm). This increasing sensitivity of the chemical shifts of the C-5 of thiadiazoles studied to the changes in the substituent in aryl group in comparison with the shifts of C-5 atom in 1,3,4-oxadiazoles is caused by the higher aromaticity of thiadiazole ring than the oxadiazole one. The increasing of the aromaticity results in more effective coupling of π-electrons system of both C═N bonds with phenyl ring electrons. The chemical shifts of both carbon atoms of thiadiazole unit show correlation with global Hammett constants, although for C-2, the r^2 values are slightly smaller. Analysis of the contributions inductive and resonance effects to the chemical shifts variation (dual substituent parameter treatment) has shown that on C-2 the former dominates. For C-5, these contributions are of similar importance (Table 4). In both cases, the ‘goodness of fit’ of dual substituent parameter correlation, judged by f parameter ($f = \mathrm{SD/RMS}$), indicates the good correlation ($f = 0.10$ and 0.13 for C-2 and C-5, respectively). As for selenium and oxygen containing analogs,[47,49] the opposite effects of the substituent electronic character on C-2 and C-5 chemical shifts may be explained by the redistribution of the C═N bond electron density caused by its polarization and, in consequence, an increase in the diamagnetic effects on C-5. This mechanism is more effective in highly delocalized electron systems of aromatic thiadiazole and selenadiazole rings, in comparison with non-aromatic oxadiazoles.[49]

The C-1′ chemical shift range of the compounds studied is 16.40 ppm, which is smaller than for 1,3,4-oxadiazoles (18.45 ppm).[49] The analysis of the correlation of ^{13}C δ values with Hammett constants shows the smaller contribution of resonance effects in comparison with that of oxadiazoles, caused by the coupling with π-system of heterocyclic ring (the resonance effects are not stopped on C-1′ atom, but are transferred via extended coupled electron systems on the second part of the molecule). The value of f parameter (0.11) indicates good correlation.

The Z factors, calculated for 1,3,4-thiadiazo-2-yl substituents from the values obtained for the studied substances are $Z_1 = 1.2 \pm 0.6$, $Z_2 = -0.7 \pm 0.6$, $Z_3 = 0.6 \pm 0.3$ and $Z_4 = 2.3 \pm 1.2$. These values are intermediate between those for oxadiazol-2-yl and selenadiazo-2-yl group.

The ^{15}N NMR parameters

The observed ^{15}N signals are by about 68 ppm high-frequency shifted in comparison with those obtained for substituted 1,3,4-oxadiazoles (e.g. −86.77 and −73.44 vs −17.96 and −5.43 ppm for N-3 and N-4 of 2-phenyl-substituted 1,3,4-oxa and 1,3,4-thiadiazole, respectively).[49] The chemical shifts of N-4 are very close to the value reported for unsubstituted 1,3,4-thiadiazole (−7.9 ppm).[53] The ^{15}N NMR data obtained for the molecules studied are very similar to those presented previously for selena analogs, the signal of the selenium containing compounds is less than 5 ppm shifted.[47] The ranges of the chemical shifts of N-3 and N-4 in the molecules studied are 16.74 and 2.87 ppm, respectively. As follows from a comparison with previously published data,[47,49] the chemical shift of nitrogen atom in thiadiazole ring is less sensitive to electronic properties of substituent than that of selenadiazole, but more sensitive than that of oxadiazoles. This is a result of the higher aromaticity of 1,3,4-thiadiazole than that of the oxy analogs (and lower than that of selenadiazoles). It causes the stronger π-electron systems coupling and more effective transfer of the electronic effects from phenyl to chalcogenediazoyl ring. Both nitrogen atoms show the chemical shift–Hammett constant relationship, but for N-4 atom, the r^2 parameter is much smaller than for N-3. The origin of this effect is unclear if compared with results presented earlier for oxadiazoles and selenadiazoles – for these compounds the differences in r^2 values obtained for N-3 and N-4 are less than 0.1, whereas for thiadiazoles, the difference is 0.35.

The ^{33}S parameters

The ^{33}S NMR signal of 2-phenyl-1,3,4-thiadiazole (**6**) was observed at −55 ppm as a very broad line of $\Delta\nu_{1/2} \sim 3500$ Hz. Because of the low intensity and great line width, the accuracy of chemical shift measurement was lower than 10 ppm. The spectrum of 2-(4-methoxyphenyl)-1,3,4-thiadiazole (**3**) shows a signal at −59 ppm. Because the observed substituent-induced shifts were less than the accuracy of measurement, the spectra of the other compounds were not recorded. The value obtained is similar to that reported for thiophenes (−112 ppm for 2-methylthiophene) or 2-methylthiazol (−72 ppm).[55,56]

Theoretical calculations

The calculated chemical shifts for the compounds studied are collected in Table 3. The computed bond lengths, charges (Mülliken and natural bond orbital ones) and Cartesian coordinates are presented in the Supporting Information. As follows from a comparison of the experimental and calculated values, the ^{13}C chemical shifts are slightly overestimated by the calculation methods, but an excellent correlation between these values was found ($r^2 = 0.85$–0.99; see Table 4 for details). The highest difference between δ_{calc} and δ_{exp} is observed for C-2 (about 10 ppm), whereas the smallest for C-5 (less than 5 ppm). The calculated ^{15}N chemical shifts are by 20–27 ppm high-frequency shifted. If the values computed for N-3 correlate well with the experimental ones, then the correlation obtained for N-4 is very poor ($r^2 < 0.6$). The reasons for such a difference are not clear, such effects were not observed for oxa and selena analogs.[46,47,49]

Conclusions

The NMR results obtained for 2-aryl-1,3,4-thiadiazoles are similar to those published previously for oxa and selena analogs. The chemical shifts values are intermediate between those for the corresponding O and Se containing 1,3,4-chalcogendiazoles. The DFT calculations reproduce the ^{13}C chemical shifts values very well, but the observed systematic error is slightly smaller than that for 1,3,4-selenadiazoles. The differences between calculated and measured δ values of nitrogen atoms are much higher than those for carbons. Contrary to the results obtained for oxygen and selenium containing analogs, N-4 chemical shifts show very poor correlation with Hammett constants as well as calculated δ values, but the reasons for such differences are not known. The ^{33}S NMR spectra of two representative 2-aryl-1,3, 4-thiadiazoles were recorded but, because of the huge line broadening due to quadrupolar relaxation, the substituent effect was not observed.

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