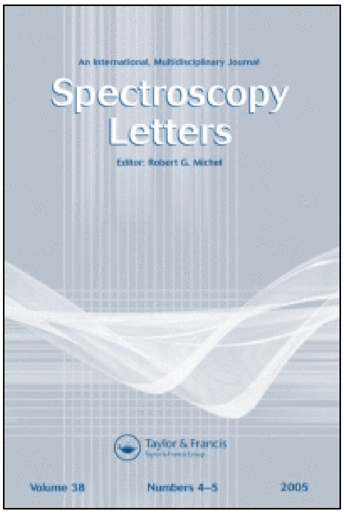

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A ^{15}N NMR STUDY OF SOME IMIDAZOLIDINE-2,4-DICHALCOGEN DERIVATIVES

Key Words : ^{15}N NMR ; HYDANTOIN DERIVATIVES ; NMR / IR CORRELATION

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ABSTRACT

The ^{15}N NMR chemical shifts and $^{1}J(^{15}N-^{1}H)$ coupling constants of a series of imidazolidine-2,4-dichalcogen (O, S) derivatives are reported.The ^{15}N NMR chemical shifts show a linear

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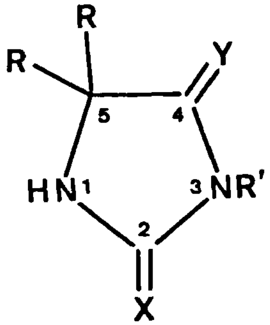
correlation with the νNH stretching vibrations. The influence of the substitution of the oxygen at C_2 and/or C_4 with the sulphur, and of the hydrogen at C_5 with the methyls and phenyls has been considered. The $^1J(^{15}N-^1H)$'s found in this series of molecules agrees well with the expected values.

INTRODUCTION

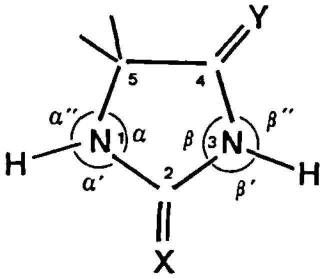
In recent years ^{15}N NMR has been proved to be a valuable tool in the study of the electronic properties of amido and thioamido groups in a variety of biologically active compounds[1] Nevertheless, little information is available on the ^{15}N NMR of imidazolidine- 2,4-dichalcogen derivatives, so that we retain it useful to examine the following compounds and to study how the different substitution affects the nitrogens.



	X	Y	R	R'
1	O	O	H	H
2	O	O	Me	H
3	O	O	Ph	H
4	O	O	Me	Me
5	S	O	H	H
6	S	O	Me	H
7	S	O	Ph	H
8	O	S	Me	H
9	S	S	Me	H
10	S	S	Me	Me

Table I

Bond lengths (A) and angles (°) around the nitrogens for some imidazolidines



Compound	2	3	5	9
N_1C_2	1.329	1.343	1.322	1.326
C_2N_3	1.380	1.406	1.393	1.397
N_3C_4	1.363	1.353	1.349	1.339
C_2X	1.227	1.218	1.642	1.648
C_4Y	1.203	1.234	1.225	1.641
α	113.5	114.2	113.4	114.1
α'	—	—	122.9	130.5
α''	—	—	123.6	115.5
β	111.8	112.6	112.6	113.4
β'	—	—	131.4	124.2
β''	—	—	116.0	122.3
Ref.	2	3	4	5

RESULTS AND DISCUSSION

^{15}N Chemical shift. The nearness of the amido and/or thioamido groups in **1-10** produces different nitrogen lone-pairs delocalization with consequent structural changes. In Table 1, the bond distances of the atoms involved in the π system are reported for **2, 3, 5,** and **9,** whose crystal structures are known [2-5]. In the same Table, the angles around the nitrogens are reported.

As one can see, the changes in the structural parameters are fairly small and consistent with the electronic effects induced by the substitution of oxygen with sulphur. Viceversa, the ^{15}N chemical shifts of N_1 and N_3 in **1-10** spread in a wide range, as shown in Table 2. The δN_1 chemical shifts are always more shielded than the δN_3's, and this well agrees with the different acidity of the two NH protons[6].

We tried to correlate the chemical shifts with the bond strengths of the NH's, measured as stretching frequencies.

The results are reported in the Figure. Compound **10** apart, the correlation calculated on all the other compounds (full line) is acceptable ($r= 0.89$). However, by eliminating compound **4** (which is N_3 methylated as **10**) and compounds **3** and **7** (which contain phenyl groups at C_5),the correlation becomes very good (dotted line, $r=0.96$).

In order to evidentiate the influence of the different substituents, we have reported the chemical shift differences ($\Delta\delta$) for some selected couples in Table 3. By examining the couples **5/1**, **6/2**, **7/3**, and **9/8**, it can be said that : i) the values of $\Delta\delta N_1$ for the

Table 2

^{15}N NMR chemical shifts, δ (ppm), and nitrogen-proton coupling constants ^1J (Hz) for **1-10**. Solvent: CD_3COCD_3/ DMSO 1:1

	δN_1	$^1J(N_1H)$	δN_3	$^1J(N_3H)$
1	-298.1	96.4	-231.5	95.5
2	-272.8	96.6	-238.0	94.7
3	-272.5	96.5	-234.7	90.3
4	-274.7	92.8	-243.0	——
5	-259.2	99.6	-211.1	97.5
6	-233.9	99.2	-216.7	97.2
7	-245.1	98.6	-215.2	*
8	-265.7	97.0	-200.7	97.3
9	-227.5	100.8	-186.5	100.5
10	-229.3	101.7	-190.9	——

Values are referred to neat nitromethane as external reference as 0.0 ppm

* Undetermined.

four couples of compounds have the same magnitude; ii) the values of $\Delta\delta N_3$ are almost half $\Delta\delta N_1$; iii) the substituents at C_5 show little effects in influencing $\Delta\delta N_1$ and $\Delta\delta N_3$. The reduced value of $\Delta\delta N_3$ for **9/8** is indicative of a smaller electron availability of N_3 towards C_4, whereas $\Delta\delta N_1$ is not affected by the substitution at C_4. In fact, the presence of the sulphur at C_4 induces a major conjugation of the

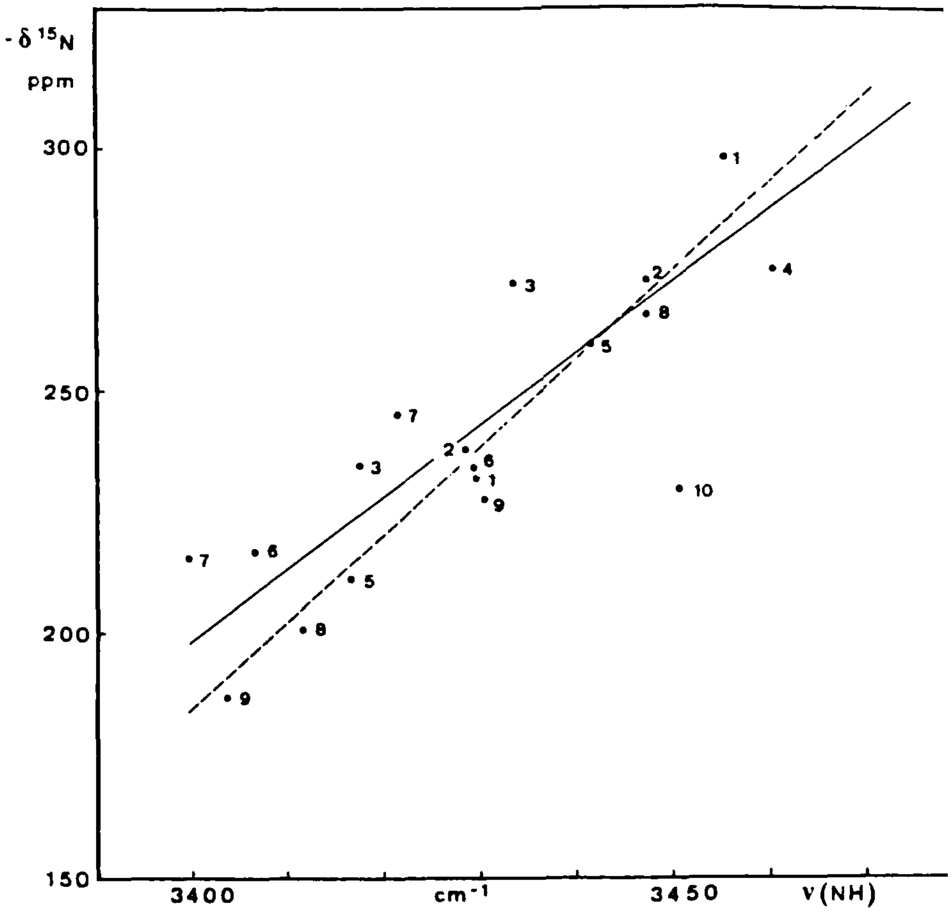


Figure Linear correlation between $\delta^{15}N$ chemical shifts and the ν(NH) stretching vibrations. The full line is calculated over all experimental points, except **10** (r = 0.89). The correlation showed by the dotted line is obtained by excluding the points **3**, **7**, **4** and **10** (see text) (r = 0.96).

Table 3.

$\Delta\delta N_1$ and $\Delta\delta N_3$ (ppm) from couples of **1**-**10**

Substitution at C_2

Couple	R	R'	X/X	Y/Y	$\Delta\delta N_1$	$\Delta\delta N_3$
5/1	H	H	S/O	O/O	38.9	20.4
6/2	Me	H	S/O	O/O	38.9	21.3
7/3	Ph	H	S/O	O/O	27.4	19.5
9/8	Me	H	S/O	S/S	38.2	14.2

Substitution at C_4

Couple	R	R'	X/X	Y/Y	$\Delta\delta N_1$	$\Delta\delta N_3$
8/2	Me	H	O/O	S/O	7.1	37.3
9/6	Me	H	S/S	S/O	6.4	30.2

Substitution at C_2 and C_4

Couple	R	R'	X/X	Y/Y	$\Delta\delta N_1$	$\Delta\delta N_3$
9/2	Me	H	S/O	S/O	45.3	51.5
10/4	Me	Me	S/O	S/O	45.4	52.1

Substitution at C_5

Couple	R / R	R'	X	Y	$\Delta\delta N_1$	$\Delta\delta N_3$
2/1	Me/H	H	O	O	25.3	-6.5
3/1	Ph/H	H	O	O	25.6	-3.2
6/5	Me/H	H	S	O	25.3	-5.6
7/5	Ph/H	H	S	O	14.1	-4.1

lone-pair of N_3 towards the N_3C_4 bond, as proved by the structural data (Table 1) and by the enhanced values of $\Delta\delta N_3$ for the couples **8/2** and **9/6**.

Their low $\Delta\delta N_1$ values are probably more related to a reduction of the conjugation of the N_3 lone pair on the C_2N_3 bond than to a precise influence of the substituent at C_4.

The simultaneous substitution at C_2 and C_4 of oxygen with sulphur (couples **9/2** and **10/4**) promotes high values of $\Delta\delta N_1$ and $\Delta\delta N_3$, with the latter being greater than expected. The $\Delta\delta$ values for the double substitution seem to obey an additive law.

The influence of the substitution at C_5 is shown by the comparison of the couples **2/1**, **3/1**, **6/5**, and **7/5**. This influence on δN_1 can be interpreted in terms of the β effect[1]. The substitution of methyls with phenyls seems to have little consequence for the N_1 shielding. As regards the N_3 nitrogen shielding, the weak influence of the substituents at C_5 can be expressed as a γ-effect[1].

^{15}N-^{1}H Coupling constants. The magnitude of the coupling between ^{15}N and directly bonded hydrogen is determined by the amount of s-character in this bond[7] according to:

$$\%s = 0.43\ {}^{1}J(NH) - 6 \qquad (1)$$

On the basis of the crystal structures of the compounds reported in

Table 1 and other similar molecules, the imidazolidine ring is practically planar, showing that the two nitrogens are sp^2 hybrids in all the considered compounds. However, the ring forces the angles α and β to values ranging within 117° and 110° (found as α and β in 3-isopropyl-5,5-dimethyl imidazolidine-2-thione-4-one), which in accordance with the relation:

$$\%s = 100 \cos\theta / (\cos\theta - 1) \qquad (2)$$

(where θ is roughly evaluated as $(360 - \alpha(\beta)/2)$ give 34.3 and 36.5 respectively as %s character of the N-H bond. On the basis of these values, the corresponding $^1J(NH)$ values calculated from (1) are 93.7 and 98.8, in which range most $^1J(NH)$ values of **1-10** fall (see Table 2). The upper limit is overcrossed by the compounds which contain one or two sulphur atoms. In this case, the higher polarizability of the C=S bond with respect to C=O increases the p-character of the C-N bonds and consequently, the s-character of the N-H bonds.

EXPERIMENTAL

Materials: Compounds **1** (Hydantoin), **2** (5,5-Dimethyl-Hydantoin), **3** (5,5-DiphenylHydantoin), **5** (2-Thiohydantoin), **7** (5,5-Diphenyl-2-Thiohydantoin) were purchased from ALDRICH. Compounds **6** (5,5 Dimethylimidazolidine-2-thione-4-one), **8** (5,5-Dimethyl-imidazolidine-2-one-4-thione) and **9** (5,5-Dimethyl-imidazolidine-2,4-dithione) have been prepared and purified according to literature[8-10]. Compound **4** (3,5,5-Trimethyl-imidazolidine-2,4-dione) was synthesized starting from 5,5-Dimethyl-hydantoin, which is methylated in position 3 by reaction with methyl iodide in a water/ethanol solution of NaOH. (Refluxing time 1 hour ; molar ratios 1:1:1) The reaction product is recrystallized from benzene after purification with activated carbon. M.P.= = 147 °C. Anal.Calcd. for $C_6H_{10}N_2O_2$: C, 50.8; H, 7.4; N, 20.0. Found: C, 50.7; H, 7.2; N, 19.7 .

Compound **10** (3,5,5-Trimethylimidazolidine-2,4-dithione) was synthe- sized by refluxing compound **8** for 2 hours with P_2S_5 (molar ratio 2.5 : 1) in tetrahydronaphthalene. The reaction product is then purified from benzene. M.P. = 171 °C. Anal.Calcd. for $C_6H_{10}N_2S_2$: C, 41.3;H, 5.8; N, 16.1. Found : C, 41.2; H, 5.6; N,16.0.

***Measurements*:** ^{15}N NMR spectra were obtained on a BRUKER WM-250 FT NMR spectrometer operating at a frequency of 25.33 MHZ ; 16 K data points were collected over a spectral width of 8900 Hz with an acquisition time of 0.91 sec. .The spectra were recorded by using neat liquid nitromethane as an external reference, and chemical shielding values are reported relative to nitromethane at 0.0 ppm.

The ^{15}N NMR spectra of compounds **1-10** were measured in a dry solution of acetone-d_6/DMSO 1 : 1 in 10 mm sample tubes, using the polarization transfer technique INEPT. The 1/4 J value used for time delays was 2.63 ms ; the INEPT sequence was repeated after 2.5 sec. The N-Me signals in **8,10** were recorded by the inverse gated technique, with a 20° angle pulse and a repetition time of 10 sec.. All the spectra were taken using 1 M solutions containing 0.05 M $Cr(acac)_3$ in acetone-d_6/DMSO 1 : 1 mixture.

The i.r. spectra (3500-3150 cm^{-1}) were recorded using a Perkin Elmer 983 instrument in CH_2Cl_2 solutions in KBr cells for liquid with a pathway of 1 mm. The envelopes of the bands due to the $\nu(NH)_{free}$ have been deconvoluted with a program written for an HP 85 calculator .

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