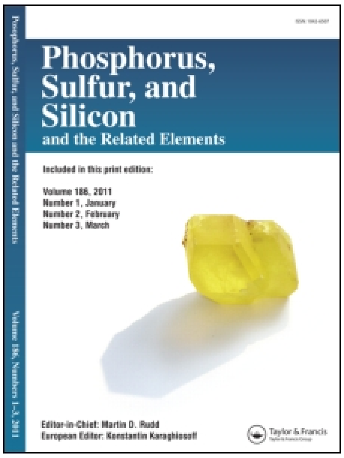

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^{1}H AND ^{13}C N.M.R. STUDIES ON SOME PENTAATOMIC RINGS CONTAINING THE THIO AND SELENO-AMIDO GROUPS

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^1H AND ^{13}C N.M.R. STUDIES ON SOME PENTAATOMIC RINGS CONTAINING THE THIO- AND SELENO-AMIDO GROUPS

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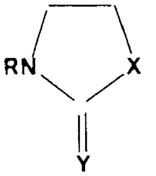
The ^1H and ^{13}C nmr spectra have been recorded on pentaatomic rings, having formula $\overline{RN\cdot CH_2\cdot CH_2\cdot X\cdot C}=Y$ (where for R = H, X = NH, NMe, NEt, CH_2, S; for R = Me, X = NMe; for R = Et, X = NEt; Y = S, Se) in $CDCl_3$ solutions.

A simple calculation on the σ-skeleton, based on the method reported by Del Re, has been carried out on the thionic derivatives (Y = S).

A satisfactory linear relation between the chemical shifts of the carbons not interacting with the π-system and their calculated σ-charges has been found.

INTRODUCTION

For some time, we have focused our interest on the chemistry of heterocyclic pentaatomic molecules with nitrogen, oxygen, sulfur and selenium as heteroatoms, considering the following compounds with the thio- or seleno-amido group



R = H, Me, Et
X = NH, NMe, NEt, O, S, Se, CH_2
Y = S, Se

in view of their biological interest. The aims of these investigations were both to emphasize the change in chemical behaviour on substituting thioketonic sulfur with selenium and to point out the influence of the X substituent on the chemical properties of the thio- and seleno-amido groups. In particular, the donor ability of Y towards transition metal ions and its oxidability to disulfide or diselenide have been considered. In order to answer the above problems, various techniques have been used. Infrared spectroscopy,[1-6] mainly based on "selenation,"[7] has allowed to locate the vibrations related to $>C{=}Y$ and, consequently, to study the influence of X on the π-system of $RN\cdot CY\cdot X$. These results have also been corroborated by N.C.T. analysis,[8] carried out only on some rings, by dipole moment studies[9] and UPS spectroscopy.[10] However the stability constants of the adducts of these molecules with the

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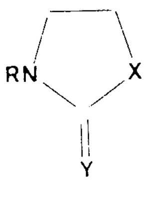
molecular iodine[11] proved to be the most sensitive index for measuring the charge density on the Y atom. As the increase of charge density on Y determines a higher stability of the adducts, oxidation to disulphide or diselenide becomes easier, as seen for transition metal reduction in high oxidation states.[12-13]

In this paper we wish to report the results of an ^{1}H and ^{13}C NMR study, carried out on the following sulfur and selenium derivatives:

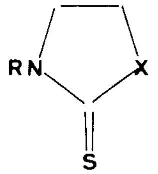


Y = S	R	X	Y = Se
1	H	NH	2
3	H	NMe	4
5	H	NEt	6
7	Me	NMe	8
9	Et	NEt	10
11	H	CH_2	12
13	H	S	14

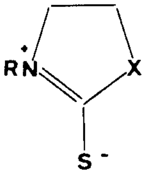
in order to correlate the nuclear resonances with the other chemical properties previously investigated.

RESULTS AND DISCUSSION

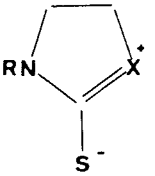
All the compounds here considered are given in Figure 1, where every carbon is labelled with the ^{13}C chemical shifts, relative to the sulfur and selenium derivatives (selenium in parentheses). As expected, the C(2) resonances show that this carbon is the most deshielded of all and we can recognize the influence of the X substituent in ring on its chemical shifts. In fact, the imidazolidine-2-thiones (**1**, **3**, **5**, **7**, **9**) show the absorption in the 182.0–183.9 ppm range, whereas **11** shows it at 186.9 ppm and **13** at 202 ppm. The highest shielding of the imidazolidines is in good agreement with the contribution of (B) and (C) to the electronic delocalization[14]



(A)



(B)



(C)

whereas in **11** the (C) contribution is practically negligible. The major deshielding of **13** with respect to **11** is due both to the inductive effect of the endo-sulfur and to a certain contribution of (C) to the resonance. The shielding of C(2) is increased in the selenium parent compounds, this indicating that the contribution of the zwitterionic forms to the resonance is higher in the selenium than in the sulfur series. On the other hand the increase of the importance of the zwitterionic forms on passing through the amido-, thio- and seleno-amido compounds has been widely discussed on the basis of several techniques by many authors.[15-17] In particular, this trend was previously found by us in **1–14**[1-2,4] and similar pentaatomic rings[3,5,6] by infrared spectroscopy and by their stability constants with molecular iodine.[11]

The influence of the X substituent in ring is also verified on the C(4) and C(5) atoms. These resonances in **13** and **14** are attributed according to *Sathyanarayana*,[18]

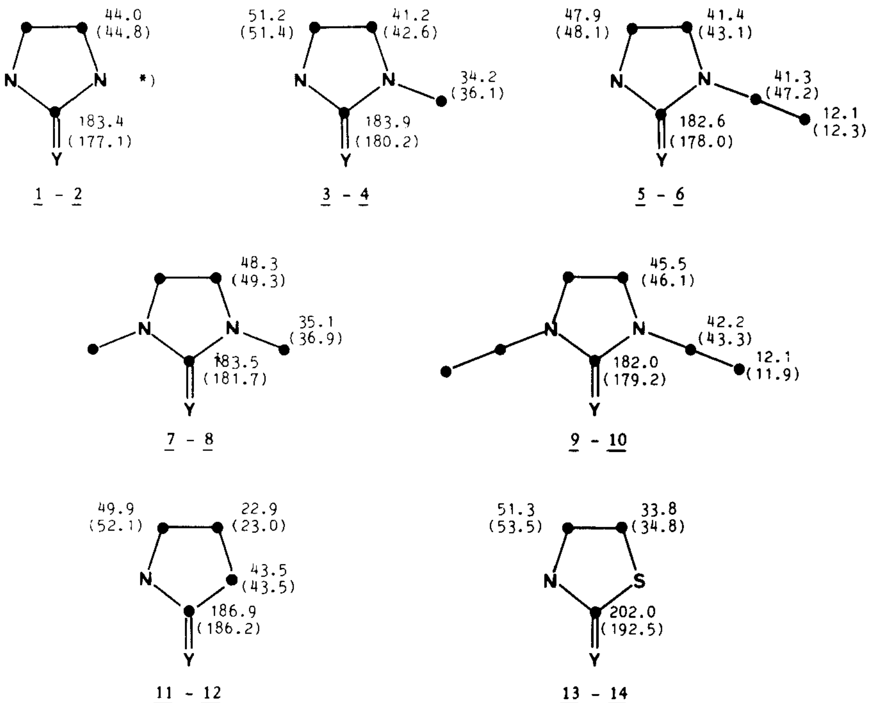


FIGURE 1 ^{13}C chemical shifts of the thionic and selonic derivatives in $CDCl_3$, (selonic in parentheses). These resonances are measured in d_6-DMSO since **1** and **2** are insufficiently soluble in $CDCl_3$.

whereas in **11** and **12** there is some doubt as to the attributions of C(4) and C(5). For this reason, the ^{13}C chemical shifts of all the compounds have been tentatively correlated with the charge densities calculated by CNDO/2, previously reported in literature,[19] and collected in Figure 2. As can be seen, this correlation is not satisfactory. Alternatively, we tried a more simplified calculation by considering only the σ bonds, using the method outlined by Del Re[20-21] (see Figure 3). The calculated

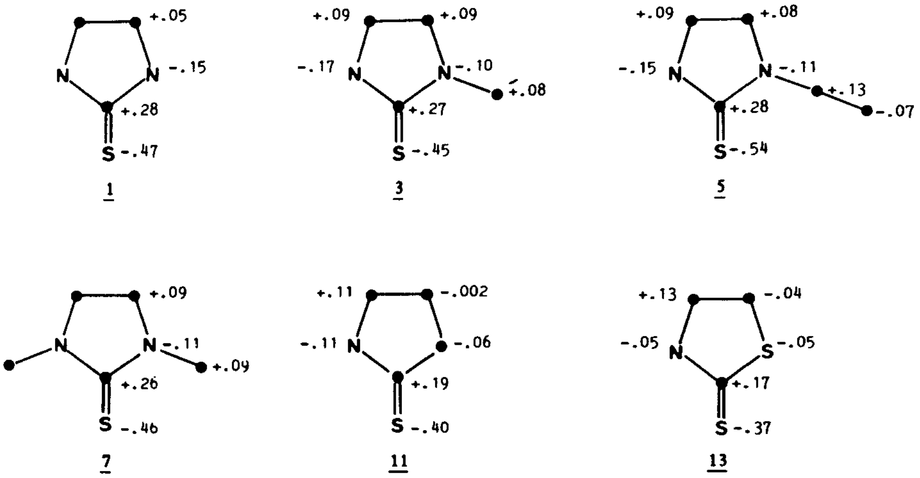


FIGURE 2 CNDO/2 charges of the heavy atoms for the thionic derivatives reported by Ref. 19.

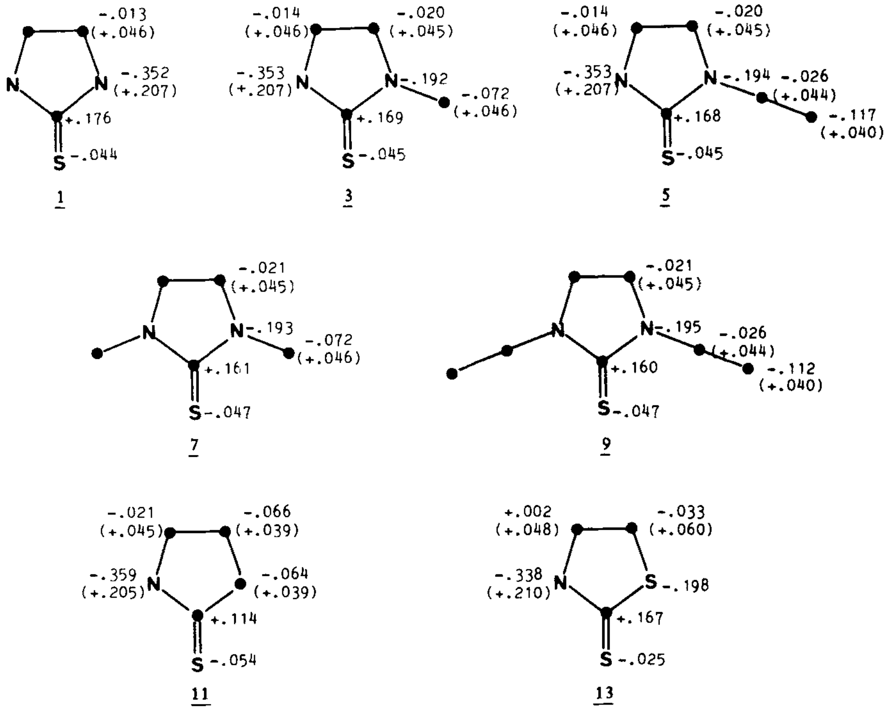


FIGURE 3 σ-charges calculated on the thionic derivatives by Del Re method. The values in parentheses are referred to the hydrogens.

charges on the carbons unaffected by the π-system are related to the experimental chemical shifts in Figure 4. Such a correlation seems to be quite good and for this reason we have assigned the resonance in **11** and **12** as reported in Figure 1.

As far as the influence of the sulfur substitution with the selenium atom, the C(2) resonances fall at lower fields in the selenium derivatives, while all the other carbons undergo a deshielding effect.

In the *N,N'*-disubstituted imidazolidines (**7–10**), it is possible to emphasize the different effect of the methyl or ethyl group. In fact, in accordance with the inductive effect, C(4) and C(5) are deshielded in the methyl more than in the ethyl derivatives.

On the basis of the calculated σ-charges, the assignments of the carbon resonances in **3–6** are made as reported in Figure 1, and these agree well with the inductive effect of the alkyl group, which affect C(5) more than C(4). However, if one compares the resonances between the mono- and di-substituted imidazolidines, the assignment might be reversed by analogy.

The ^{1}H chemical shifts of H—N are collected in the Table I together with the infrared vibration frequencies νNH. An empirical correlation between the ^{1}H chemical shifts and the vibrational frequencies of NH has been reported recently by *Sathyanarayana*,[18] who only used νNH values obtained on the solid samples instead of those recorded on the same solutions used for the n.m.r. spectra. In fact, the infrared spectra of **3–6** and **11–14** recorded in $CDCl_3$ or $CHCl_3$ exhibit two distinct peaks above 3100 cm^{-1}, due to the free and hydrogen bonded νNH, called ν_{free}NH and ν_{ass}NH respectively. There seems to be a rough correlation[20] between the chemical shifts and both νNH. In the last column of Table I the ΔνNH (= ν_{free}NH −

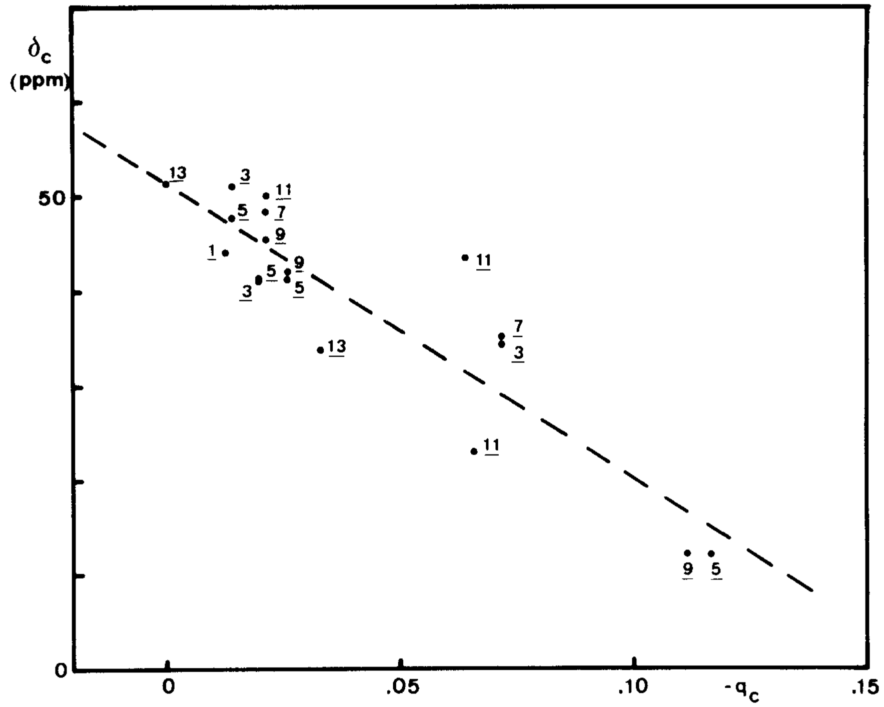


FIGURE 4 Linear correlation between the chemical shifts of the carbon having only σ bonds and their charge densities calculated by Del Re method. The correlation coefficient is 0,903.

ν_{ass}NH) are also reported; these values are indicative of the strength of the hydrogen-bonding.[1,23] The NH resonances of the selenium compounds show a higher acidity than the corresponding sulfur ones.

The chemical shifts of the protons bonded to the carbons are collected in Figure 5. As expected, the $CH_2(4)$ hydrogens are the least affected by the X substituent and their resonances range in a narrow interval, i.e. 3.54 to 3.76 ppm in **1–12**. The previous assignment[18] of $CH_2(4)$ resonances in **13** and **14** at 4.01 and 3.96 ppm seems to be in contrast with the above mentioned observation, while the reversed assignment gives 3.56 and 3.52 ppm for $CH_2(4)$ in **13** and **14**, values which agree with the whole series. The charges on the hydrogens in **13** (see Figure 3) are in good agreement with this assignment; in fact the $CH_2(5)$ hydrogens must be more deshielded

TABLE I

^{1}H chemical shifts and vibrational frequencies of NH

Compound	δ(ppm)	ν_{free}NH	ν_{ass}NH	$\Delta\nu$NH
3	6.2	3460	3240	220
4	6.6	3460	3230	230
5	6.3	3457	3233	224
6	6.5	3457	3225	232
11	8.9	3413	3153	260
12	9.5	3404	3155	249
13	8.3	3404	3150	254
14	8.7	3398	3130	268

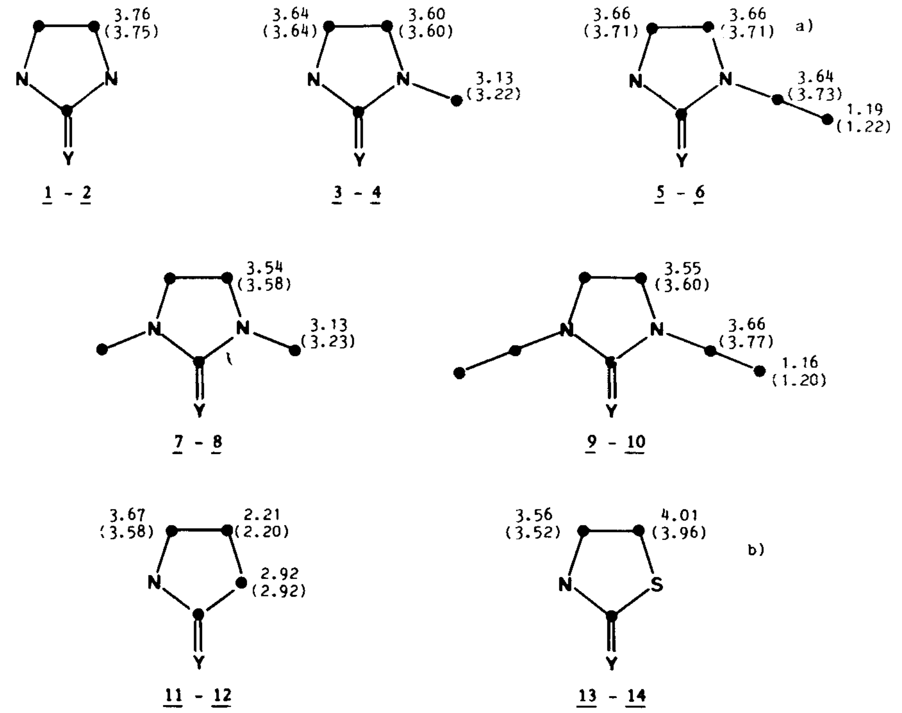


FIGURE 5 ^1H resonances of the hydrogens bonded to the carbons for the thionic and selonic derivatives in $CDCl_3$, (selonic in parentheses).
(a) The multiplets of the two CH_2 in ring can not be distinguished and the reported resonances are referred to the mean values. (b) The resonances for **14**, reported in the Sadtler Standard Spectra Catalogue (28807 M) and in Ref. 18, are reversed with respect to the present assignments.

than $CH_2(4)$ since they have a greater positive charge. It is interesting to point out that the Del Re calculation also justifies the assignments made for the ^{13}C chemical shifts, since C(4) is more positive than C(5).

The $CH_2(5)$ hydrogen resonances sensitively change on passing from the pyrrolidines (**11–12**) to thiazolidines (**13–14**), whereas the imidazolidines (**1–10**) show intermediate values. In spite of the higher electronegativity of nitrogen with respect to sulfur, which should require a major deshielding in the imidazolidines, this sequence is still justified in terms of the σ-charges on the $CH_2(5)$ hydrogens, which are +.039, +.045 ÷ +.046 and +.060 for **11**, **1–9** and **13** respectively.

Finally, the substitution of the sulfur with the selenium atom does not sensitively change the n.m.r. resonances of the hydrogens bonded to the carbons, both in and out of the ring.

EXPERIMENTAL

The preparation and purification of all the compounds have been previously described in literature.[4,24–32]

The n.m.r. spectra have been recorded with a Varian FT-80-A spectrometer operating at a nominal frequency of 80 MHz for the ^1H and 20 MHz for ^{13}C at a probe temperature of ~32° in $CDCl_3$ solutions, except for **1** and **2** which were recorded in DMSO-d_6. The chemical shifts were digitally computed using TMS as internal reference. In the case of the multiplets, only the mean value has been reported.

The infrared spectra were recorded on a Perkin-Elmer mod. 325 spectrophotometer on the same solutions used for the n.m.r. experiments.

The σ-charge calculation has been carried out on the thionic derivatives with a program written for the Del Re method, using the parameters reported in Refs. 20 and 21.

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