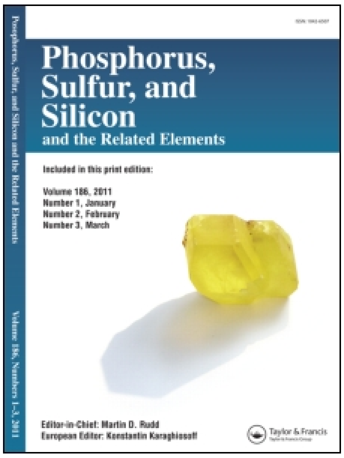

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N.M.R. SPECTRA OF 5,5-DIMETHYLIMIDAZOLIDINES HAVING O, S OR Se ATOMS IN 2,4

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N.M.R. SPECTRA OF 5,5-DIMETHYLIMIDAZOLIDINES HAVING O, S OR Se ATOMS IN 2,4.*

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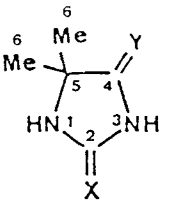
The ^{13}C N.M.R. spectra of a series of 5,5-dimethyl 2,4-dichalcogeno substituted imidazolidines are reported. The ^{13}C chemical shifts are assigned by means of a CNDO/S calculation. On the whole the shielding effect of the di-homochalcogeno atoms on C-2 and C-4 increases in the order Se $\leqslant$ S $\ll$ O while for the di-hetero atoms no regular trends have been found. On the contrary the resonance of C-5 inside the ring moves downfield keeping one chalcogen atom constant and substituting the oxygen with sulphur and selenium.

INTRODUCTION

Recently we have synthesized[1] the following homogeneous series of molecules having the hydantoin skeleton:



Y \ X	O	S	Se
O	**(1)**	**(3)**	**(5)**
S	**(2)**	**(6)**	**(8)**
Se	**(4)**	**(7)**	**(9)**

with the aim of using them as ligands towards transition metal ions. In fact, they may act as neutral or negative ligands to yield inner complexes,[2] and both exo-chalcogen atoms *X* and *Y* can compete to or simultaneously coordinate the metal ions.[3] These different behaviours depend on the π-electron distribution over the —HN—CX—NH—CY— moiety, as properly verified by considering the acid properties of the NH hydrogens[4] and the donor abilities of *X* and *Y* in forming charge transfer adducts with molecular iodine.[5] However, also the nuclear magnetic

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resonances of ^{13}C are related to the π-electron system. There have been a large number of papers reporting ^{13}C N.M.R. chemical shift data in a variety of heterocyclic compounds. Generally, these papers either deal with the assignments of chemical shifts, or correlate them with structural parameters to give structural information in solution as, for example, about the existence of tautomeric equilibria. For this reason, we now report on a ^{13}C N.M.R. study of imidazolidines (**1**)–(**9**).

RESULTS AND DISCUSSION

In order to assign the ^{13}C chemical shifts of (**1**)–(**9**) we have employed the charge densities calculated on the carbons by CNDO/S and reported in the Table together with the ^{13}C resonances. The assignments are made by assuming a linear correlation between the calculated charge densities and the chemical shifts. As seen for similar molecules, this is a valid procedure and works satisfactorily also with less sophisticated calculations than CNDO/S.[6,7] The linearity of this dependence is shown in Figure 1, where some regularities are shown, i.e. the carbon-2 is the most deshielded atom and the resonances of the carbons fall at lower fields on passing from oxygen to sulphur to selenium, as also found for a series of substituted azolidines-2-one, -2-thione and -2-selone.[6,7] Both observations are well shown up by comparing the chemical shifts at C-2 and C-4 of (**1**), (**6**) and (**9**).

In preceding studies carried out on (**1**)–(**9**) we have found good correlations between the stretching frequencies of the NH's and the charges on the hydrogens[4] and between the stability constants of the adducts of (**2**)–(**9**) with molecular iodine and the charge densities of the exo-donor atom.[5] There, we were able to correlate the

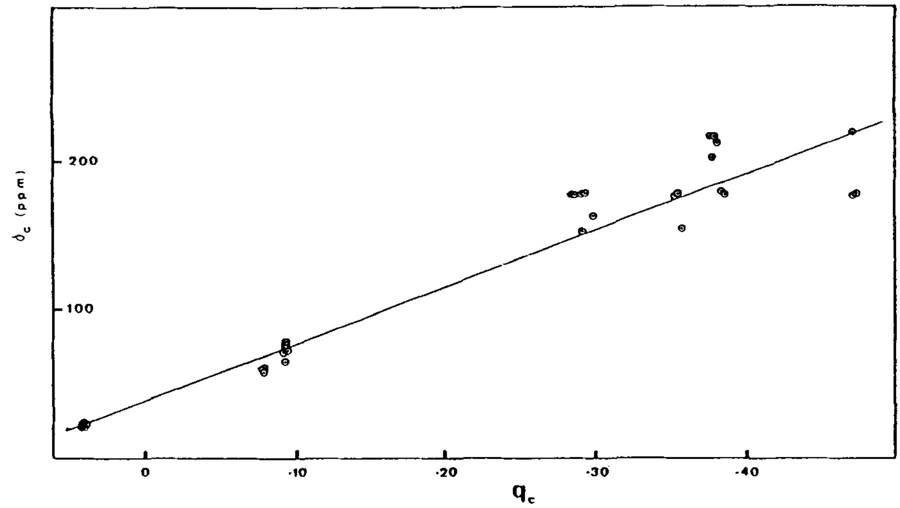
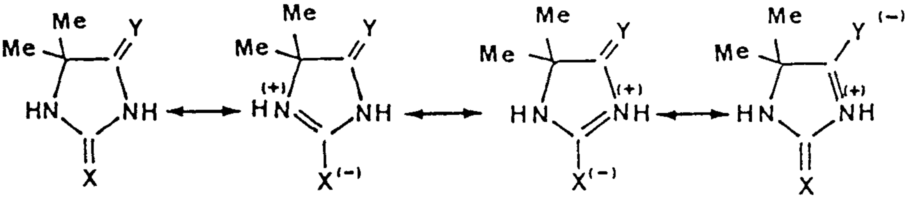


FIGURE 1 Linear correlation between the chemical shifts of the carbons and their charge densities calculated by CNDO/S : $\delta_c = 387q_c + 41$. The correlation coefficient is 0.98.

stretching frequencies of NH's with the exo-substitution at C-2 and C-4, and the results were rationalized using the following resonance equilibrium:



Nevertheless, if we try to point out the influence of the exochalcogen atoms at C-2, leaving the exo-atoms at C-4 unchanged, simple trends are not found. The same occurs by keeping constant the exo-atom at C-2 and varying that at C-4. However, the resonances of C-5 exhibit a regular trend on passing from oxygen, to sulphur and to selenium. In fact for (**1**), (**2**) and (**4**) where we vary the exo-atom at C-2 leaving the oxygen at C-4, they increase from 57.0, to 60.0 and 60.9 ppm respectively. For (**1**), (**3**) and (**5**) where we vary the exo-atom at C-4, leaving the oxygen at C-2, the resonances are 57.0, 65.3 and 72.2 ppm. These values indicate that the substitution of O with S and Se deshields the C-5, and that this effect is more consistent for the exo-atom at C-4 than at C-2. Similar trends can be found for all the other series obtained fixing *X* or *Y*. Also the two methyl groups are sensitive to *X* and *Y*, but their variations, as shown in Table I, are very small.

EXPERIMENTAL

The compounds (**1**)–(**9**) have been prepared and purified according to literature.[1]

The N.M.R. spectra have been recorded with a Varian FT 80-A spectrometer operating at a nominal frequency of 20 MHz for ^{13}C at about 32°C in d_7-DMF. The chemical shifts were digitally computed using TMS as internal reference.

The quantum-mechanical calculations were performed on a UNIVAC 1100, using CNDO/SHIFT/UV program (QCPE n° 382) with CNDO/S parametrization.

TABLE I

q_c CNDO/S charges (a.u.) and δ_c ^{13}C chemical shifts (p.p.m.) of (**1**)–(**9**)

Compound	q_c				δ_c			
	C-2	C-4	C-5	C-6*	C-2	C-4	C-5	C-6
(**1**)	.4739	.3581	.0781	−.0392	177.2	154.1	57.0	22.6
(**2**)	.3840	.3550	.0770	−.0391	178.6	177.3	60.0	21.6
(**3**)	.4714	.2912	.0923	−.0387	176.1	153.7	65.3	26.1
(**4**)	.3863	.3534	.0768	−.0391	177.3	176.3	60.9	20.3
(**5**)	.4705	.2992	.0939	−.0387	218.2	162.7	72.2	26.5
(**6**)	.3780	.2859	.0915	−.0387	202.0	177.3	71.2	25.3
(**7**)	.3809	.2836	.0915	−.0387	211.8	177.1	74.3	25.2
(**8**)	.3758	.2939	.0928	−.0386	216.7	179.1	77.0	25.5
(**9**)	.3786	.2915	.0928	−.0386	216.6	177.6	79.3	24.9

*These charges are averaged on the two methyl groups.

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