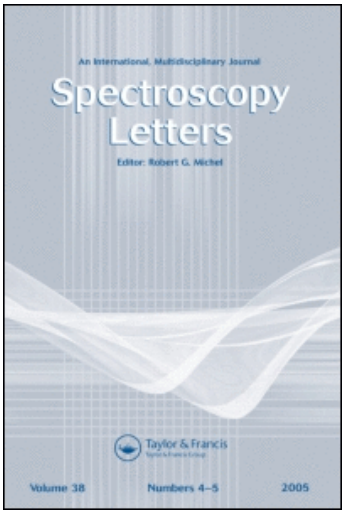

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A ^{13}C NMR Study of 3,5,5-Trimethyl-4-Oxoimidazolidine-2-Thione and 3,5,5-Trimethyl Imidazolidine-2,4-Dithione Complexes with Molecular Diiodine

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A ^{13}C NMR STUDY OF 3,5,5-TRIMETHYL-4-OXO-IMIDAZOLIDINE-2-THIONE AND 3,5,5-TRIMETHYL IMIDAZOLIDINE-2,4-DITHIONE COMPLEXES WITH MOLECULAR DIIODINE.

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Key Words : ^{13}C NMR, HYDANTOIN DERIVATIVES, CYCLIC THIOAMIDES, C.T. COMPLEXES WITH I_2

ABSTRACT

The ^{13}C NMR spectra of C.T. complexes between donors containing a thioamido group and diiodine are reported. The rapid exchange of donor between the free and the adduct state makes the variation in the position of the resonance depend on the ratio of these two species.

Data are comparatively examined with those of the related molecules: 5,5-dimethyl-4-oxoimidazolidine-2-thione and 5,5-dimethylimidazolidine-2,4-dithione. The influence of diiodine on the ^{13}C chemical shifts shows that I_2 affects C(2) more than C(4) and confirms that, in the two compounds with two C=S groups, the interaction of I_2 takes place with the sulphur bonded to C(2).

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INTRODUCTION

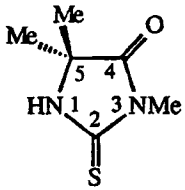
In these last years[1-6] we have been studying the reaction

$$D + I_2 \rightleftharpoons D \cdot I_2 \qquad (1)$$

where D is a donor molecule and $D \cdot I_2$ its charge transfer-complex with diiodine. The donor molecules employed in these studies were pyrrolidines, oxazolidines, thiazolidines, imidazolidines, benzoxazoles, benzothiazoles, benzoimidazoles and hydantoins, all characterized by having at least one thio- or seleno-amido group in a pentaatomic ring. The main purpose was to measure the influence of the chemical environment on the donor properties of the chalcogen atom of the thio- or seleno-amido group by determining the formation constants and the thermodynamic parameters of reaction (1).

This type of research was first stimulated by the interest of these molecular compounds in studies on hyperthyroidism[7,8]. More recently, the sulphur-iodine charge-transfer complexes have proved to be promising molecules for their electrical properties [9-11]. This has led us to further study of sulphur-diiodine and selenium-diiodine complexes both in solution and in the solid state, and very recently[12] we have described the crystal structures of four neutral charge-transfer molecular compounds formed between some imidazolidine derivatives used as donors (i.e. 5,5-dimethylimidazolidine-2,4-dithione, 5,5-dimethyl-4-oxoimidazolidin-2-thione and 5,5-dimethyl-4-oxoimidazolidin-2-selone) and molecular diiodine.

In order to extend the investigation on charge-transfer complexes and to study the influence of diiodine on the donor molecule, the results of a ^{13}C NMR study on the two selected molecules 3,5,5-trimethyl-4-oxoimidazolidine-2-thione (**1**) and 3,5,5-trimethylimidazolidine-2,4-dithione (**2**) will be reported and the data comparatively examined with those of compounds (**3**) and (**4**) already published.



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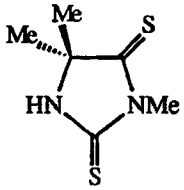

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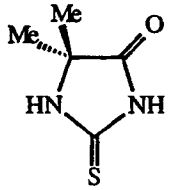

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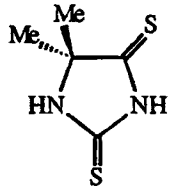

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EXPERIMENTAL

Compound Preparation. 3,5,5-Trimethyl-4-oxoimidazolidine-2-thione[6] **(1)**, 3,5,5-trimethylimidazolidine-2,4-dithione[13] **(2)**, 5,5-dimethyl-4-oxoimidazolidine-2-thione[14] **(3)**, and 5,5-dimethylimidazolidine-2,4-dithione[14] **(4)** have been prepared and purified according to literature.

Measurements. The studies were all carried out in methylene chloride. For each donor, several solutions having the same concentration of donor with increasing amounts of diiodine were recorded. Likewise, the maximum diiodine/donor molar ratio employed was typically 4 to shift the equilibrium reaction (1) towards the complex formation.

The ^{13}C NMR spectra were recorded at the temperature of 20°C on a Varian FT NMR spectrometer VXR 300, operating at 75,4 MHZ frequency. $CDCl_3$ (77.00 ppm) was employed as the external reference.

The i.r. spectra (3500-200cm^{-1}) on the solid samples were recorded as KBr discs, using a Perkin Elmer 983 instrument connected with a Perkin-Elmer 7500 Data Station.The spectra in solution (3600-3100 cm^{-1}) were recorded in KBr cells for liquid with a pathway of 0.05 or 1mm.

Data treatment. From equilibrium (1), the ^{13}C observed chemical shift, δ (ppm), is given by

$$\delta = [D]\,\delta^{\circ}_{D}/[D]^{\circ} + [DI_2]\,\delta^{\circ}_{DI2}/[D]^{\circ} \qquad (2)$$

where [D] and [DI_2] are the equilibrium concentrations of the free donor and the complex respectively, $[D]^{\circ}$ the analytical concentration of the donor, δ°_{D} and δ°_{DI2} the chemical shifts of the donor and the complex respectively.

From equation (2)

$$\delta = \delta^{\circ}_{D} + \Delta\delta^{\circ}[DI_2]/[D]^{\circ} \qquad (3)$$

where $\Delta\delta^{\circ} = \delta^{\circ}_{DI2} - \delta^{\circ}_{D}$. The plots of $(\delta-\delta^{\circ}_{D})[D]^{\circ}$ *versus* $[DI_2]$ for C(2), C(4) and C(5) are reported in Figure 1. From the slopes of the straight lines the values of $\Delta\delta^{\circ}$ can be estimated. Since the variations of the chemical shifts of C(8)/C(9) and NMe on passing from the free ligand to the adducts are very small (see Table 1), they have not been reported in the Figure.

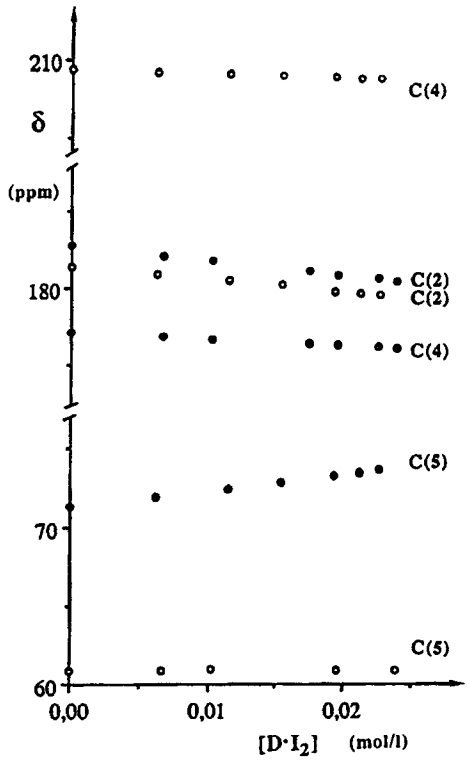


Figure 1. The ^{13}C NMR chemical shifts of C(2), C(4) and C(5) for 1 (•) and 2 (o) respectively as a function of the C.T. complex concentration $[D{\cdot}I_2]$. All points have the same concentration of donor and increasing amounts of diiodine: [1] = $2.67{\cdot}10^{-2}$M; [2] = $2.61{\cdot}10^{-2}$M; CH_2Cl_2 solution; t=20°C. The spectrophotometric formation constants used in the calculation of $[D{\cdot}I_2]$ have been taken from Ref.6.

Since the experimental design in the NMR measurements cannot be as good as that obtained from Uv-visible data*, we have optimized only the chemical shifts of the 1:1 complexes using the spectrophotometric formation constants[6,9] to calculate the concentration of DI_2 for each solution.

* *Solubility reasons and high concentrations of the donor, necessary for the NMR experiments, make it impossible to explore large ranges of the saturation fraction.*

RESULTS AND DISCUSSION. As one can see from Figure 1, the ^{13}C NMR resonance signals for carbons C(2), C(4) and C(5) of **(1)** and **(2)** vary linearly with $[D \cdot I_2]$. The C(2) and C(4) signals decrease, while C(5) increases.

The ^{13}C chemical shifts of the free donors and the extrapolated shifts of the 1:1 complexes are reported in Tab. 1 together with those of the corresponding compounds **(3)** and **(4)** and their adducts[12].

In all compounds the complex formation shows its influence mainly on carbon C(2) in accordance with the fact that this atom is bonded to the sulphur binding diiodine. The upfield shift of C(2) is to be explained with a higher degree of conjugation of the lone pair of the nitrogens towards this carbon atom. In order to highlight the effect of the sulphur-coordination of diiodine on the structural parameters of the free ligand, we report some selected bond lengths[12,15] of the

Table 1. ^{13}C NMR chemical shifts (ppm) of compounds 1-4 and their 1:1 C.T. complexes.

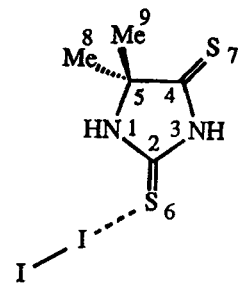
Compound	C(2)	C(4)	C(5)	C(8)-C(9)	N-Me
1	182.72	177.06	60.87	23.95	27.33
1·I_2	180.12	175.96	62.68	23.83	27.51
Δδ°	-2.60	-1.10	1.81	0.12	0.18
2	181.39	209.38	71.35	27.98	32.35
2·I_2	179.20	208.77	73.88	28.10	32.24
Δδ°	-2.19	-0.61	2.53	-0.12	0.11
3*	180.30	177.23	63.49	23.85	---
3·I_2*	178.20	175.60	64.92	23.72	---
Δδ°	-2.10	-1.63	1.14	-0.13	
4*	179.27	210.31	74.35	27.78	---
4·I_2*	177.48	208.91	75.78	27.77	---
Δδ°	-1.79	-1.40	1.43	**	

* Ref. 12 **No detectable variations were found.

compounds **4**[15] and **4·I_2**[12], for which the crystal structures have been solved (see Table 2; Δ =bond length in the adduct - bond length in the free donor).

Table 2. Bond lengths (Å) for the hydantoin skeleton of **4** and its adduct.

	4	**4·I_2**	Δ
N(1)-C(2)	1.326	1.307	- 0.019
C(2)-S(6)	1.648	1.678	+0.030
C(2)-N(3)	1.397	1.372	- 0.025
N(3)-C(4)	1.339	1.351	+0.012
C(4)-S(7)	1.641	1.636	- 0.005
C(4)-C(5)	1.525	1.512	- 0.013
C(5)-N(1)	1.461	1.487	+0.026
C(5)-C(8)	1.516	1.515	- 0.001
C(5)-C(9)	1.516	1.534	+0.014



4·I_2

The shortening of N(1)-C(2) and C(2)-N(3) in **4·I_2** indicates that the two nitrogens increase their lone pair conjugation toward C(2). At the same time N(3)-C(4) and C(5)-N(1) undergo lengthenings. By comparing the changes of the two C=S bonds at C(2) and C(4), it can be seen that only C(2)=S(6) undergoes a valuable lengthening, whereas C(4)=S(7) becomes shorter by only 0.005Å, since it is practically a double bond.

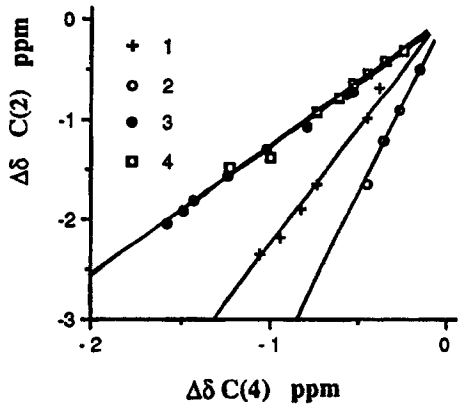
From Table 1, by comparing the chemical shift values of the free compounds and their adducts (compare the couples **1/3**, **2/4**, **1·I_2/3·I_2** and **2·I_2/4·I_2**), the effect of the N(3)H hydrogen substitution with a methyl group can be shown. The observed differences are of the order of 2-3 ppm for C(2) (upfield) and C(5) (downfield) and very small for C(4) both in the free and coordinated ligands. These small changes, verified on methylation, are coherent with the small variations of the stability constants of the adducts of **1-4**[6] (201 and 171dm^{3}mol^{-1} for **1-3** ; and 143 and 126dm^{3}mol^{-1} for **2-4**; t=25°C; CH_2Cl_2)

From the crystal structures[12] of 5,5-dimethylimidazolidine-2,4-dithione-diiodine, 5,5-dimethylimidazolidine-2,4-dithione-bis(diiodine), 5,5-dimethyl-4-oxoimidalidine-2-thione-diiodine and 5,5-dimethyl-4-oxoimidazolidine-2-selone-

diiodine, it was evident that in the solid state there is a hydrogen bonding interaction between the NH and the iodine bonded to the sulphur. This hydrogen bonding interaction can be shown in by i.r. spectroscopy. In fact, the ν(NH) vibration frequencies, recorded in CH_2Cl_2 solution, are lowered from 3437 and 3430 cm^{-1} to 3385 and 3373cm^{-1} in the adducts of **1** and **2** respectively.

In Table 1, the $\Delta\delta^\circ$ values (i.e. the chemical shifts of the adduct minus the chemical shifts of the free donor) are also reported. These data show that there is a close connection between the presence of the methyl group and the reduced value of $\Delta\delta^\circ$ in C(4) for both compounds **1**·I_2 and **2**·I_2 with respect to **3**·I_2 and **4**·I_2.

Fig. 2 shows the values of Δδ (i.e. the chemical shifts measured on solutions at different donor/diiodine ratios minus the chemical shifts of the free donor) of C(2) as a function of Δδ of C(4) for the four compounds. The slopes are all greater than 1, which means that I_2 affects C(2) more than C(4) also in compounds **2** and **4** where two C=S groups are present.



Although the 1:1 model fitted the experimental absorbances for compounds **2** and **4** very well[6], it was not possible to prove that the interaction of I_2 was achieved only with S(6) and not with S(7). Now, the similar slopes (1,28 and 1,29) for compounds **3** and **4** respectively indicate that in compound **4** the group C(4)S(7) does not bind diiodine at least in the experimental conditions used. Finally, Fig.2 clearly shows that the methyl group bonded to N(3) does not affect the chemical shifts of C(2), but in some way buffers the changes of the chemical shifts on C(4), induced as a consequence of diiodine coordination, and the slopes for compounds **1** and **2** are 2.34 and 3.59 respectively.

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