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Charge-Transfer Complexes between Some *S*-Methylated Derivatives of 5,5-Dimethyl-2,4-dithiohydantoin and Molecular Diiodine. A UV-Visible, IR, FT-Raman, and ^{13}C NMR Study

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ABSTRACT

Equilibrium constants (K) and thermodynamic parameters for the charge-transfer complexes between diiodine and Δ^3*-4-S-methyl-5,5-dimethylimidazolidine-2-thione (***1***), 2-S-methyl-5,5-dimethylimidazolidine-4-thione (***2***), and* Δ^1*-*Δ^3*-2S-methyl-4-S-methyl-5,5-dimethylimidazolidine (***3***) have been determined in* CH_2Cl_2 *by UV-Visible spectroscopy. Depending on the solvent polarity, compound* **2** *exists as a* Δ^1 *or* Δ^2 *tautomer; both the tautomers are present in* CH_2Cl_2*. Compounds* **1** *and* **2** *act as good donors (K = 11,000 ± 800 and 640 ± 21* $dm^3\ mol^{-1}$*, 25°C, respectively) owing to the presence of a thioamidic group in the molecule, whereas in compound* **3***, the N-coordination causes a strong reduction of the formation constant (K = 14.6 ± 0.8* $dm^3\ mol^{-1}$*, 25°C). The high difference between the stability constants of* **1** *and* **2** *has been ascribed to an intramolecular hydrogen bonding between NH and the bonded iodine, which can be possible only for* **1***. Additional spectroscopic data (FT-Raman, NMR) enables a deeper understanding of the mutual interaction between donors and diiodine.*

INTRODUCTION

The study of the inhibition of the thyroid gland by compounds containing a thioamido group has received much attention in recent years [1–4]. The results showed that the formation constant K of the adduct ($D \cdot I_2$), where D is a donor molecule,

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

is a useful tool in the selection of compounds that may have pharmacological significance, as it is well correlated with the antithyroid activity *in vivo* [5–7].

Our studies on the evaluation of the equilibrium constant of Reaction 1 for different classes of compounds, all of which contain at least one thio- or selenoamido group [8–14], have allowed us to make the following remarks: (a) selenium compounds bind diiodine far more strongly than the sulfur compounds; (b) for the same donor atom, the K values strongly depend on the chemical environment and are spread over a very large interval; and (c) a small variation in the charge density on the donor atom produces a remarkable change in K. The search for new compounds, with potential pharmaceutical importance, capable of binding diiodine or acting on enzyme thyroid peroxidase has led us to synthesize three *S*-methylated derivatives of 5,5-dimethyl-2,4-dithiohydantoin (**4**) with the aim of studying the different donor abilities of

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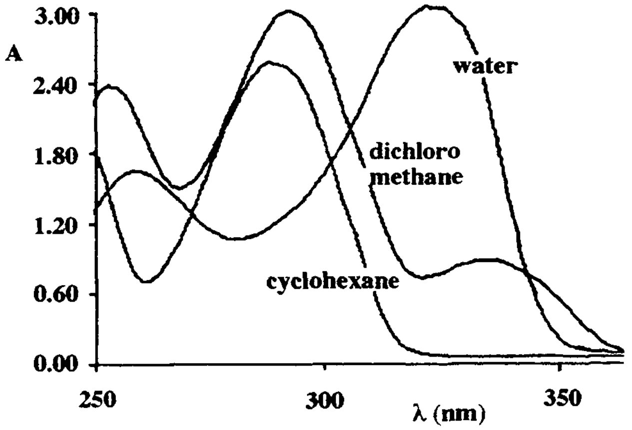
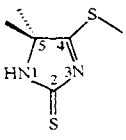


FIGURE 1

1, 2, and 3 toward I_2 in CH_2Cl_2 solution. The results are compared with those previously reported for compound **4** [14].



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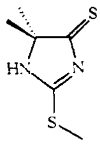

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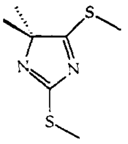

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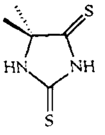

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RESULTS AND DISCUSSION

Compounds 1–3 contain different donor atoms that may compete in the coordination of I_2. Each donor possesses sulfur and nitrogen atoms characterized by a different capability to transfer electronic charge density to the acceptor molecule (I_2). Moreover, as previously verified for 2-*S*-methyl-5,5-dimethylimidazolidin-4-one [15], compound **2** exists as Δ^1 and/or Δ^2 tautomers (annular desmotropy) [16,17], depending on the solvent polarity. The ultraviolet spectra of **2** recorded in water, CH_2Cl_2, and cyclohexane are reported in Figure 1.

Apolar solvents such as cyclohexane stabilize the Δ^1 tautomer, while solvents such as water stabilize the Δ^2 tautomer, in accordance with the dipole moment values calculated both by PM3 and AM1 methods [18]. As can be seen from Figure 1, both tautomers are present in CH_2Cl_2. Compound **3**, as expected, shows only one UV band that slightly shifts on passing from water to cyclohexane (see the Experimental section). On the other hand, compound **1**, as also found for **2**, shows a remarkable change in its UV spectrum with change of solvent polarity (see the Experimental section). On the basis of molecular structure, it is possible to exclude the presence of a desmotropic equilibrium for **1**, but not that of a thioketo-enolic equilibrium. However, no experimental evidence has been found for the thioenolic tautomer in solution [19].

In the experimental conditions used for the determination of the K's, all the charge-transfer complexes exhibit an isosbestic point between the visible band of I_2 and its blue-shifted band (see Figure 2). This fact excludes the presence of a $D \cdot 2I_2$ adduct but not the contemporary interaction of different donor sites with I_2.

The K and ϵ values with their relative standard deviations calculated at five different temperatures, together with the thermodynamic parameters for equilibrium 1, are reported in Table 1.

Both the K's and the ΔH's for $\mathbf{1} \cdot I_2$ and $\mathbf{2} \cdot I_2$ complexes show that **1** and **2** are good donors toward diiodine. These values clearly indicate the thiocarbonyl sulfur to be the donor atom and as expected, are greater than those found for 5,5-dimethylimidazolidine-2,4-dithione (**4**) (K = 143 $dm^3\ mol^{-1}$; 25°C; CH_2Cl_2; $\Delta H = -30$ Kj mol^{-1}) [12].

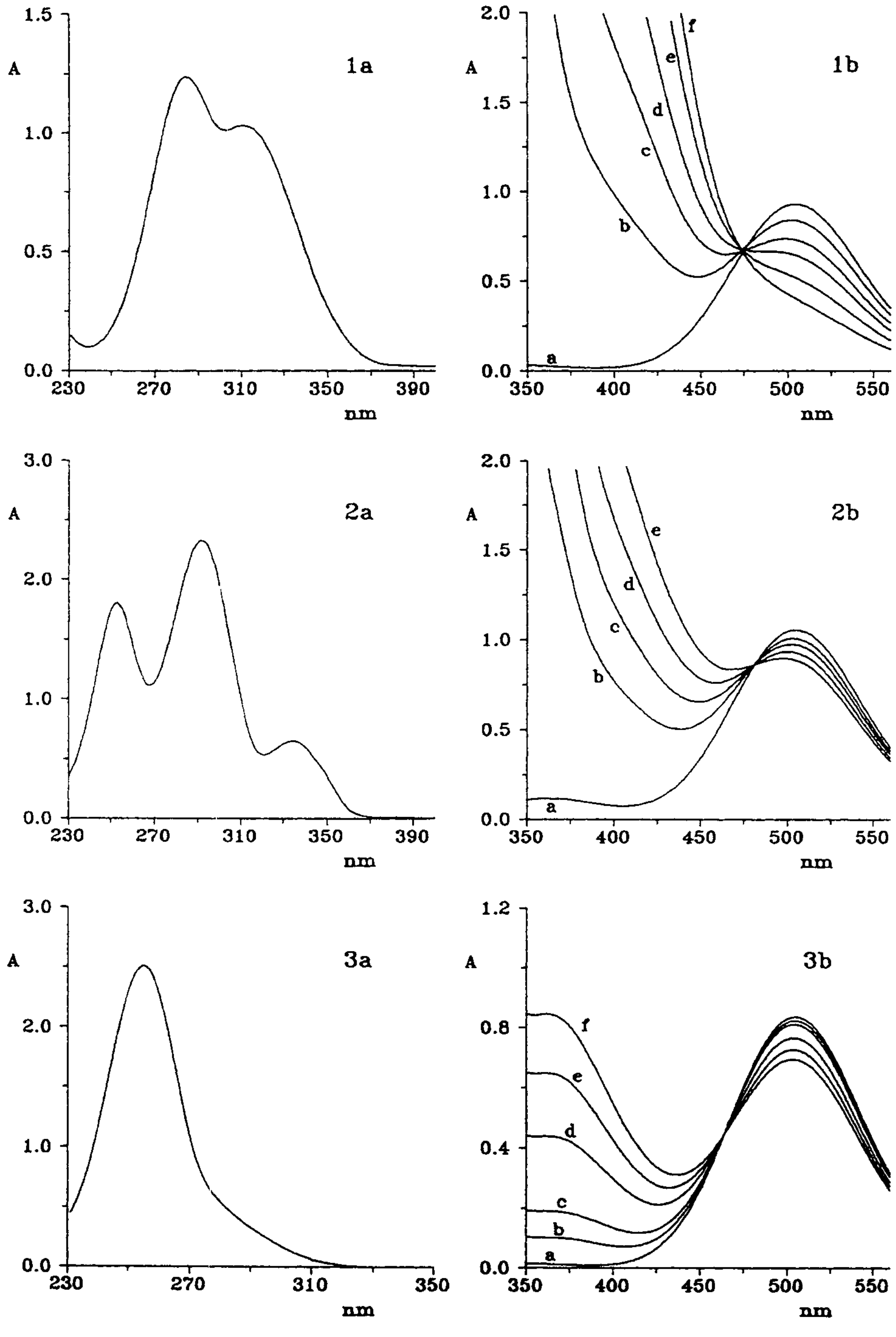
In fact, the monosubstitution of C–S–Me to C(2)=S or C(4)=S in **4** increases the charge electron density on the ring and favors its partial displacement on to the remaining C=S group. In compound **3**, the double substitution of the thioketonic sulfurs with S–Me produces a strong reduction in both K and ΔH values with respect to compound **4**, in accordance with the lower donor abilities of thioether sulfurs and nitrogens.

The measured ^{13}C NMR chemical shifts of carbons C(2), C(4), C(5), Me/Me, and SMe for compounds **1**–**4**, together with those of their calculated 1:1 adducts with I_2, are reported in Table 2. The values previously reported for compound **4** are included for comparison [20].

As verified on other thiohydantoin derivatives [14,20], $S \cdots I_2$ coordination has the effect of increasing the shielding of the carbon bonded to the donor sulfur as a consequence of charge withdrawal from the ring toward C=S; C(2) in **1** and C(4) in **2** are then shielded by δ = 4.99 and 4.38, respectively.

All the other carbons are generally deshielded, except C(5) in **2**, which undergoes a shift of δ = 2.76 toward higher fields. It is important to point out that for **2** the shielding of C(5) occurs contemporaneously with a very high (δ = 21.49) deshielding of C(2). In consequence of the interaction of C(4)=S sulfur with diiodine, electronic charge is attracted toward C(4) from both sides of the ring; the lone pairs of the two nitrogen atoms lower the conjugation toward C(2) and move toward C(4), thus producing a shielding of C(5) and a deshielding of C(2). In the compound $\mathbf{3} \cdot I_2$, all the carbons are deshielded. The shifts of 3.62 and 0.87 for C(2) and C(4), respectively, seem to indicate N(1) as the coordinating atom. With the aim of ascertaining the site of coordination, the ^{14}N NMR spectra of **3** and of a solution containing **3** and diiodine in a 1:1 molar ratio were recorded in CH_2Cl_2 solution. Only an unresolved broad signal at $\delta = -92.2$ is present in the free donor spectrum, which shifts to -130.5

FIGURE 2



in the presence of diiodine; this result seems to indicate that both nitrogens can be involved in the coordination. In this case, the *K* value must be considered as the sum of the two *K*'s relating to the two parallel equilibria involving both N(1) and N(3) [12].

In order to explain the very high difference in *K* values between *N,N'*-dimethyl-4-oxo-imidazolidine-2-thione and *N,N'*-dimethyl-4-thioxo-imidazolidine-2-thione in comparison with the values found for their *N*-monomethylated or unmethylated derivatives [14,20], a hydrogen bonding interaction between the NH hydrogen and the coordinated iodine was invoked and experimentally proved by IR spectroscopy. In fact, the ν(NH) stretching vibration frequencies of the free donors shift toward lower values in the presence of diiodine. The hydrogen bonding interaction has also been proven to operate in the solid state, since many crystal structures of adducts of thiohydantoin de-

TABLE 1 Molar Extinction Coefficients ϵ (dm^3 mol^{-1} cm^{-1}) at the 6 Wavelengths λ (nm) Used for the Calculation, Association Constants K (dm^3 mol^{-1}), and Sums of the Squared Deviations (χ^2) for the Reaction between Compounds **1**, **2**, and **3** with I_2[a]

	Compound 1		*Compound 2*		*Compound 3*	
	λ	ϵ	λ	ϵ	λ	ϵ
15°C	430	3000(95)	420	4410(38)	410	2820(40)
	420	3900(120)	410	5550(35)	400	3460(33)
	410	4800(140)	400	6850(43)	380	4470(40)
	400	5800(130)	390	8520(68)	370	4600(50)
	390	6800(110)	380	10800(170)	360	4540(53)
	380	8200(140)	370	13800(260)	350	4770(39)
	$K = 24000(3000)$		$K = 1200(48)$		$K = 21(1)$	
	$\chi^2 = 0.225$		$\chi^2 = 0.756$		$\chi^2 = 0.125$	
	λ	ϵ	λ	ϵ	λ	ϵ
20°C	430	3050(88)	420	4330(33)	410	2800(35)
	420	4000(113)	410	5440(34)	400	3470(32)
	410	4900(130)	400	6730(50)	380	4460(40)
	400	5800(122)	390	8400(77)	370	4610(50)
	390	6900(110)	380	10600(170)	360	4530(52)
	380	8400(128)	370	13700(260)	350	4800(40)
	$K = 16000(1500)$		$K = 900(37)$		$K = 17.5(0.8)$	
	$\chi^2 = 0.184$		$\chi^2 = 0.689$		$\chi^2 = 0.078$	
	λ	ϵ	λ	ϵ	λ	ϵ
25°C	430	3070(80)	420	4340(37)	410	2790(31)
	420	4950(99)	410	5430(35)	400	3470(31)
	410	4800(113)	400	6740(44)	380	4440(42)
	400	5700(108)	390	8470(68)	370	4580(48)
	390	6900(101)	380	10900(110)	360	4550(50)
	380	8500(124)	370	14300(230)	350	4790(40)
	$K = 11000(800)$		$K = 640(21)$		$K = 14.6(0.8)$	
	$\chi^2 = 0.143$		$\chi^2 = 0.407$		$\chi^2 = 0.056$	
	λ	ϵ	λ	ϵ	λ	ϵ
30°C	430	3110(76)	420	4320(39)	410	2780(38)
	420	4000(94)	410	5400(38)	400	3450(30)
	410	4800(106)	400	6730(47)	380	4450(32)
	400	5800(103)	390	8500(69)	370	4620(43)
	390	7000(205)	380	10970(88)	360	4520(48)
	380	8800(146)	370	14500(160)	350	4800(42)
	$K = 7600(600)$		$K = 475(12)$		$K = 12.8(0.9)$	
	$\chi^2 = 0.199$		$\chi^2 = 0.199$		$\chi^2 = 0.067$	
	λ	ϵ	λ	ϵ	λ	ϵ
35°C	430	3210(88)	420	4300(43)	410	2770(52)
	420	4200(118)	410	5400(44)	400	3440(48)
	410	5100(143)	400	6750(53)	380	4450(36)
	400	6200(143)	390	8600(76)	370	4670(50)
	390	7500(120)	380	11200(85)	360	4468(54)
	380	9400(167)	370	14900(130)	350	4890(38)
	$K = 5200(350)$		$K = 357(8)$		$K = 10.6(0.9)$	
	$\chi^2 = 0.193$		$\chi^2 = 0.136$		$\chi^2 = 0.023$	
	$\Delta H = -56.8(0.3)$ Kj mol^{-1}		$\Delta H = -45.3(0.7)$ Kj mol^{-1}		$\Delta H = -24.8(0.8)$ Kj mol^{-1}	
	$\Delta S = -13(1)$ j mol^{-1} K^{-1}		$\Delta S = -98(2)$ j mol^{-1} K^{-1}		$\Delta S = -61(2)$ j mol^{-1} K^{-1}	
	$r = 1.000$		$r = 1.000$		$r = 0.999$	

[a] Standard deviations in parentheses.

TABLE 2 ^{13}C NMR Chemical Shifts (δ) of Compounds **1–4** of the Calculated 1:1 CT Complexes with Diiodine and Their Differences $\Delta\delta^{\circ}$ (=Chemical Shift of the Adduct − Chemical Shift of the Ligand)

Compound	*C(2)*	*C(4)*	*C(5)*	*Me/Me*	*S(1)Me*	*S(2)Me*
1	192.76	200.45	72.93	25.62	—	13.89
$1 \cdot I_2$	187.77	205.91	76.21	25.86	—	14.90
$\Delta\delta^{\circ}$	−4.99	5.46	3.28	0.24		1.01
2	160.25	221.25	80.83	26.58	12.64	—
$2 \cdot I_2$	181.74	216.87	78.07	28.11	16.54	—
$\Delta\delta^{\circ}$	21.49	−4.38	−2.76	1.53	3.90	—
3	171.86	204.44	82.64	25.56	14.36	14.90
$3 \cdot I_2$	175.48	205.31	82.92	26.06	15.67	15.13
$\Delta\delta^{\circ}$	3.62	0.87	0.28	0.50	1.31	0.23
4	179.27	210.31	74.35	27.78	—	—
$4 \cdot I_2$	177.48	208.91	75.78	27.77	—	—
$\Delta\delta^{\circ}$	−1.79	−1.40	1.43	−0.01	—	—

rivatives with I_2 show an N–H···I interaction [14,21]. For **1**, the ν(NH) stretching frequency shifts from 3427 (free donor) to 3367 cm^{-1} (adduct), with a Δν of 60 cm^{-1}, very similar to those found for **4**, where the shifts were 61 and 64 cm^{-1} for N(1) and N(3), respectively [20]. These values of Δν(NH) are slightly lower with respect to the value of 70 cm^{-1} found for N-ethyl-imidazolidine-2-thione ($K \approx$ 80,000 $dm^3\ mol^{-1}$ at 25°C; CH_2Cl_2) [1]. These findings indicate that the contribution of intramolecular hydrogen bonding to the stabilization of the adducts is almost the same in compounds containing the –NH–CS– thioamido group. Compound **2** shows only one ν(NH) stretching frequency at 3398 cm^{-1} that is not shifted by the complex formation; in this case, absence of the intramolecular hydrogen bond seems to indicate that **2** prefers to bind diiodine as the Δ^2 tautomer. Finally, the greater value of ΔH in $\mathbf{1} \cdot I_2$ (-56.8 ± 0.3 Kj mol^{-1}) with respect to that of $\mathbf{2} \cdot I_2$ (-45.3 ± 0.7 Kj mol^{-1}) might be ascribed to hydrogen bond formation.

FT-Raman spectroscopy has nowadays gained great importance [22–31] in the study of adducts with diiodine, since it is sensitive to the lengthening of the *I–I* bond induced by the coordination. In fact, the stretching frequency of I_2 (209 cm^{-1} in CH_2Cl_2 solution) shifts toward lower energies when a donor pours a fraction of its electronic charge on the σ^* antibonding orbital of I_2 and, in agreement with the MO description [32], induces a lowering of the *I–I* force constant. The measured values of ν(*I–I*) and the calculated formation enthalpy of **1–4** (for 1:1 model), together with those of N-ethylimidazolidine-2-thione [1] and 1,3,5,5-tetramethylimidazolidine-2,4-dithione [14], which have been included in order to enlarge the range of ΔH values, are pictured in Figure 3. The data are well interpolated by a second-order polynomial equation ($r = 0.99$).

This result is in accordance with the fact that both ΔH and ν(*I–I*) are related to the strength of the donor-diiodine interaction. This correlation can be useful to calculate the strength of the donor-diiodine interaction (ΔH values) in CH_2Cl_2 solution only on the ground of the ν(*I–I*) stretching frequency.

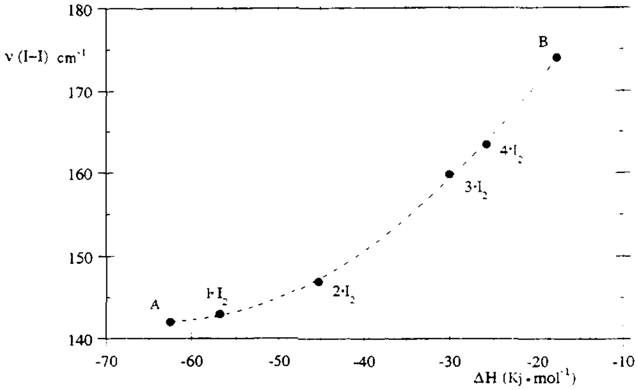


FIGURE 3

EXPERIMENTAL

Materials

All reactions of air- and water-sensitive materials were performed in flame-dried glassware under an atmosphere of nitrogen. Air and water sensitive solutions were transferred by use of hypodermic syringes or double-ended needles. Diiodine was purified by sublimation from *KI*. Δ^3-4-S-Methyl-5,5-dimethylimidazolidine-2-thione (**1**) and 5,5-dimethylimidazolidine-2,4-dithione (**4**) were prepared according to the literature [33,34]. For **1**, the spectral properties were in good agreement with those previously reported; however, we also recorded the UV spectra in water and cyclohexane: UV λ_{max} (log ε) (water, [**1**] = $2 \cdot 10^{-4}$ M): 290 nm (4.07); (cyclohexane, [**1**] = $2 \cdot 10^{-4}$ M): 275 (4.07), 312 nm (3.98). In order to make the attributions to the ^{13}C NMR signals of **1** (see the Spectrophotometric Measurements and Data Treatment section), we synthesized its $-SCD_3$ deuterated derivative with the same procedure as for **1** [33]. Δ^3-4-*S*-Deuteromethyl-5,5-dimethylimidazolidine-2-thione, which was obtained in 17% yield starting from **4**, was as follows: mp: 191–192°C. IR (KBr): ν 3250 (m), 2985 (m), 2928 (m), 2235 (w), 1510 (s), 1475 (s), 1453 (s), 1376 (m), 1368 (w), 1320 (w), 1144 (s), 1082 (s), 970 (w), 942 (w), 700 (w), 590 (bw), 549 (w), 515 (w), 425 (w). Anal. calcd for $C_6H_7D_3N_2S_2$; found (%): C (40.6) 41.0; N (15.8) 16.0; S (36.2) 36.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 200.68 (m, C(4)), 192.25 (d, ^2J (C, NH) = 5.5 Hz, C(2)), 73.59 (m, C(5)), 25.81 (dq, ^1J (C, H) = 130.7 Hz, ^3J (C, NH) = 4.4 Hz, $(CH_3)_2C-$), 13.44 (septuplet, ^1J (C, D) = 21.98 Hz, $-SCD_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.45 (s, 6H), 9.5 (brs, NH). The preparations of Δ^2-2-*S*-methyl-5,5-dimethylimidazolidine-4-thione (**2**) and Δ^1-Δ^3-2-*S*-methyl-4-*S*-methyl-5,5-dimethylimidazolidine (**3**) have been reported previously [33,35,36]. Since only a very concise description of the preparation was reported, without any yields or physical and spectroscopic characterizations of the compounds [35], the syntheses of **2** and **3** were improved by the following procedures.

Δ^2-2-S-methyl-5,5-dimethylimidazolidine-4-thione (2)

Methyl iodide (1 mL, 0.015 mol) was added to a solution of 5,5-dimethylimidazolidine-2,4-dithione (**4**) (2.4 g, 0.015 mol) in methanol (30 mL). The reaction mixture was maintained under reflux for 4 hours and then partially concentrated by evaporation at room pressure. Diethyl ether was added to the obtained solution (10 mL), until formation of a yellow solid occurred, and this was isolated by filtration. An aqueous 5% solution of $NaHCO_3$ (50 mL) was added to the yellow solid (3.54 g), and the obtained suspension was stirred for 15 minutes at room temperature. *Δ^2-2-S*-methyl-5,5-dimethylimidazolidine-4-thione (**2**) (2.06 g, 79% yield; the yield reported in Ref. [33] for the synthesis of **2** using a more complex procedure is 80.4%) was obtained after filtration. This compound was homogeneous to TLC analyses and had the following physical constants.

Mp: 168–169°C (Ref. [35]: 168°C; Ref. [33]: 171–172°C). IR (KBr): ν 3055 (m), 2972 (m), 2925 (m), 2859 (w), 1513 (s), 1451 (m), 1372 (w), 1325 (s), 1283 (s), 1203 (s), 1107 (s), 986 (m), 965 (m), 955 (m), 880 (w), 647 (w), 543 (m), 512 (m) cm^{-1}. Anal. calcd for $C_6H_{10}N_2S_2$; found (%): C (41.3) 41.6, H (5.8) 5.9, N (16.1) 16.2, S (36.8) 37.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.61 (s, 3H), 1.45 (s, 6H). UV λ_{max} (log ϵ) (water, [**2**] = $2 \cdot 10^{-4}$ M): 258 (3.92), 324 nm (4.18); (cyclohexane, [**2**] = $2 \cdot 10^{-4}$ M): 249 (3.97), 290 nm (4.11).

Δ^1-Δ^3-2-S-methyl-4-S-methyl-5,5-dimethylimidazolidine (3)

An aqueous solution 2 N NaOH (15 mL) and methyl iodide (2 mL, 0.032 mol) was added to a solution of 5,5-dimethylimidazolidine-2,4-dithione (**4**) (2.4 g, 0.015 mol) in ethanol (30 mL). The mixture was stirred at room temperature for 48 hours, and then the ethanol was evaporated under reduced pressure. The aqueous emulsion obtained was extracted with $CHCl_3$. The organic extract was washed with water until neutrality had been achieved and then dried and concentrated under reduced pressure. The residue (mp = 35–40°C) was purified by flash chromatography on silica gel, using $CHCl_3$ as eluent to give **3** as a pale yellow oil (2.22 g, 87% yield); in the literature, this compound has been reported as a solid with mp 35°C [35]. **3** was homogeneous to TLC analyses and had the following physical constants.

IR (CsI): ν 2976 (m), 2959 (w), 2927 (m), 1546 (s), 1484 (s), 1452 (w), 1359 (w), 1315 (m), 1250 (w), 1297 (m), 1133 (s), 1071 (s), 985 (m), 907 (m), 747 (w), 696 (w), 644 (m), 522 (m), 432 (w), 322 (w), 310 (m) cm^{-1}. Anal. calcd for $C_7H_{12}N_2S_2$; found (%): C (44.6) 45.0; H (6.4) 6.7; N (14.9) 14.9; S (34.0) 34.6. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.78 (s, 3H), 1.57 (s, 6H). UV λ_{max} (log ϵ) (water, [**3**] = $1.5 \cdot 10^{-4}$ M): 260 nm (4.20); (cyclohexane, [**3**] = $1.5 \cdot 10^{-4}$ M): 253 nm (4.20).

Spectrophotometric Measurements and Data Treatment

UV-Visible measurements were carried out in CH_2Cl_2 solutions by use of a Varian model Cary 5 UV-Vis-NIR spectrophotometer equipped with a temperature controller accessory. The spectra of 12 different solutions were recorded in the 280 to 500 nm range at the temperatures of 15, 20, 25, 30, and 35°C. The reagent concentrations were chosen according to the criteria outlined by Carta et al. [37]. On condition that the donor and diiodine spectra are known, it is possible to calculate a correct absorbance value (A_s) proportional to the adduct concentration

$$A_s = A_{exp} - \epsilon_{I2}[I_2]_0 - \epsilon_D[D]_0 \qquad (2)$$

where A_{exp} is the measured absorbance at the different wavelengths, ϵ_{I2} and ϵ_D the molar extinction coefficients of I_2 and the donor, respectively, and $[I_2]_0$ and $[D]_0$ the initial molar concentrations.

The matrix of the A_s values processed by a nonlinear least-squares method enables us to obtain both the ϵ values at the different wavelengths and the equilibrium K.

The data treatment was carried out using a program based on the assumption that the best values of K and ϵ are those that minimize the sum of the function $\chi^2 = \Sigma(A_c - A_s)^2/(N - 2)$, where A_C

and A_S are the calculated and the corrected absorbances and N is the number of data points. A detailed explanation of the data treatment is available in Refs. [38 and 39].

The infrared spectra in CH_2Cl_2 solutions were taken in the range $3600-3100\ cm^{-1}$ in a 0.2 cm pathway quartz cell, using a Perkin Elmer 983 instrument connected with a Perkin Elmer 7500 data station. The envelopes of the bands due to ν(NH) were deconvoluted with a program that treats every band as a Gaussian curve and minimizes the sum of the squared deviations between the experimental and calculated absorbances [40].

The FT-Raman spectra were recorded by means of a Bruker FRS 100 FT-Raman spectrometer, operating with a diode-pumped Nd:YAG exciting laser emitting at a 1064 nm wavelength and having a power impinging on the sample tunable up to 350 mW. The detection of the signal was made with an indium-gallium-arsenide detector operating at room temperature; all spectra were recorded at a 4 cm^{-1} resolution, down to the 50 cm^{-1} Raman shift. The CH_2Cl_2 solutions having a 1/1 molar ratio between donor and diiodine ($[I_2] = 3.5 \cdot 10^{-2}$ M) were put into 0.5 cm path length quartz cell and fitted into the compartment designed for a 180° scattering geometry.

The ^{1}H NMR spectra were recorded by use of a Varian FT-NMR spectrometer VXR 300, operating at 300 MHz frequency. TMS was employed as the external reference.

The ^{13}C NMR spectra were recorded on CH_2Cl_2 solutions at a temperature of 20°C by a Varian FT-NMR spectrometer VXR 300, operating at 75.4 MHz frequency. DMSO-d^6 ($\delta = 39.70$ ppm) was employed as the external reference. The attribution of the signals of carbons C(2) and C(4) in compound **1** required the preparation of its $-SCD_3$ deuterated analogues (see the Materials section). The $^{13}C\{^1H\}$ NMR spectra of **1** and Δ^3-4-*S*-deuteromethyl-5,5-dimethylimidazolidine-2-thione have allowed us to assign the peak at δ 192.76 to C(2) and that at δ 200.45 to C(4), since only the latter signal shows an apparently broader peak due to ^3J(C–D) coupling between C(4) and the deuterium atoms of CD_3 group. Carbon assignments in compounds **2** and **3** were made by analogy with other compounds already studied [41]. For the determination of the ^{13}C chemical shifts of the adducts, the procedure described in Ref. [20] was followed.

The ^{14}N NMR spectra were recorded at a temperature of 20°C by use of a Varian FT-NMR spectrometer VXR 300, operating at 21.6 MHz frequency. Neat $MeNO_2$ was employed as the external reference. The concentrations of donor and diiodine in CH_2Cl_2 solution were $9.0 \cdot 10^{-2}$ mol/dm^3.

Conformational Calculation

The semiempirical quantum mechanical calculations were done using the AM1 and PM3 methods as implemented in the MOPAC 6.0 quantum mechanical package [42]. The geometry of all the conformers was optimized using the PRECISE option and imposing a norm of the gradient of less than 0.1 with the keyword GNORM = 0.1. A calculation of the force constants on the optimized geometries showed that all the conformations obtained were minima in the potential energy surface, since all the force constants were positive.

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[18] The dipole moments, calculated by PM3, are 3.45, 3.97, and 7.03, 4.38 *D* for *syn*-Δ^1, *anti*-Δ^1 and *syn*-Δ^2, *anti*-Δ^2, respectively; the corresponding values obtained for 2-*S*-methyl-5,5-dimethylimidazolidin-4-one were 2.31, 2.37, and 3.33, 6.26 *D*, respectively [15]. The dipole moments of the four conformations of **2**, calculated by AM1, are 3.35, 3.55, and 6.48, 4.43 *D*, respectively.

[19] The infrared spectrum of **1** in CH_2Cl_2 solution shows

only one band at 3427 cm^{-1} due to the free ν(NH). No band around 2500 cm^{-1} attributable to ν(SH) stretching vibration is present. However, both PM3 and AM1 calculations indicate that the dipole moment of the thioketo tautomer (5.73 and 6.06 *D* for the two different calculations) of **1** is higher than that of the thioenolic tautomer (1.44 and 2.03 *D*). Probably, on lowering the solvent polarity, a redistribution of the electronic charge density occurs toward the thioketonic sulfur without proton transfer from the nitrogen to the sulfur. This could explain the change in the UV spectrum with solvent polarity.

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