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¹³C NMR, HOSE CALCULATIONS AND STRUCTURAL ANALYSES OF 3,5,5-TRIMETHYL-4-OXOIMIDAZOLIDINE-2-THIONE AND -4-THIOXOIMIDAZOLIDINE-2-ONE

Francesco Demartin^{ab}; Francesco A. Devillanova^{ab}; Angelo Diaz^{ab}; Francesco Isaia^{ab}; Vito Lippolis^{ab}; Gaetano Verani^{ab}

^a Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Cagliari, Italy ^b Istituto di Chimica Strutturistica Inorganica, Milano, Italy

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¹³C NMR, HOSE CALCULATIONS AND STRUCTURAL ANALYSES OF 3,5,5-TRIMETHYL-4-OXOIMIDAZOLIDINE-2-THIONE AND -4-THIOXOIMIDAZOLIDINE-2-ONE

FRANCESCO DEMARTIN, FRANCESCO A. DEVILLANOVA,[†]
ANGELO DIAZ, FRANCESCO ISAIA, VITO LIPPOLIS and
GAETANO VERANI

*Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Via
Ospedale 72-09124 Cagliari, Italy; Istituto di Chimica Strutturistica Inorganica,
via G. Venezian 21-20133 Milano, Italy*

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The crystal structures of 3,5,5-trimethyl-4-oxoimidazolidine-2-thione (1) and 3,5,5-trimethyl-4-thioxoimidazolidine-2-one (2) are reported and compared with the previously determined structures of 5,5-dimethylimidazolidine-2,4-dithione, 5,5-dimethyl-2-selenoxoimidazolidin-4-one, 5,5-dimethyl-4-selenoxo-2-thione and 2-thiohydantoin. (1) is orthorhombic ($a = 11.310(10)\text{\AA}$, $b = 7.326(2)\text{\AA}$, $c = 10.675(6)\text{\AA}$, $Z = 4$, space group Pnma; $R = 0.033$). (2) is orthorhombic ($a = 8.349(4)\text{\AA}$, $b = 9.719(8)\text{\AA}$, $c = 20.337(11)\text{\AA}$, $Z = 8$, space group Pbca; $R = 0.038$). In all these molecules the changes of the bond lengths and angles are coherent with the influence of the different exo-chalcogen atoms bonded to C(2) and C(4). The structural data are used for a simple harmonic oscillator calculation (HOSE model) in order to evaluate the contributions of the resonating forms and to relate them with the ¹³C NMR chemical shifts. The changes in angles around the C(sp²) atoms are discussed in terms of the Valence-Shell Electron-Pair Repulsion (VSEPR) model.

Key words: Hydantoin derivatives; imidazolidine derivatives; HOSE calculation; X-ray structure; thione compounds; ¹³CNMR.

INTRODUCTION

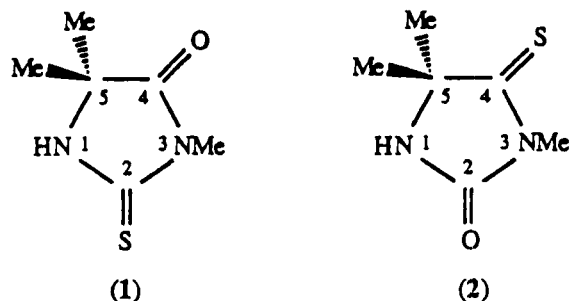
The study of the thione-thiol or selone-selenol tautomerism of molecules containing the thio- or seleno-amido entities has been an interesting subject in recent years.

X-ray analyses on a wide variety of compounds containing such groups have shown that in the solid state they are always present in the thione/selone form.^{1,2} This problem is not so well defined in solution, since this tautomerism has occasionally been reported^{1,3} and, moreover, molecules containing the thio- or seleno-amido group easily give inner complexes with metal ions.^{4–7} However, in investigations on several pentaatomic rings, all containing at least one thio- or seleno-amido group, we never found evidence for this tautomerism in solution^{8–11} and we interpreted the changes of their chemical properties by considering the influence of the exo-chalcogen atom on the π electron distribution of the ring.^{2,8–11}

Pursuant to our interest in this field, we will now report the crystal structures of the following hydantoin derivatives, i.e. 3,5,5-trimethyl-4-oxoimidazolidine-2-thione (1) and 3,5,5-trimethyl-4-thioxoimidazolidin-2-one (2) and compare their

[†]To whom correspondence should be addressed.

structural parameters with the previously reported structures of 2-thiohydantoin (=4-oxoimidazolidine-2-thione)^{2,12} (3), 5,5-dimethylimidazolidine-2,4-dithione² (4), 5,5-dimethyl-2-selenoxoimidazolidin-4-one² (5), 5,5-dimethyl-4-selenoxo-2-thione² (6).



RESULTS AND DISCUSSION

Description of the Structures

An ORTEP drawing of (1) and (2) is shown in Figures 1 and 2 respectively. While for (1) the planarity of the molecule (apart from the two methyls C(8) and C(8)^c or C(9)) is crystallographically imposed, the molecule of (2) is roughly planar, the larger displacements from planarity concerning the atoms outside the rings [O(6) = 0.037(4) Å, S(7) = 0.046(1) Å and C(11) = -0.029(5) Å]. In this molecule the exact planarity is reached only by the two groups of atoms containing the sp² carbons; the dihedral angles formed by the two planes is 2.5°.

Small deviations from planarity were also found in 2-thiohydantoin (3), 5,5-dimethylimidazolidine-2,4-dithione (4), 5,5-dimethyl-2-selenoxoimidazolidin-4-one (5) and 5,5-dimethyl-4-selenoxoimidazolidine-2-thione (6), where the dihedral angles formed by the planes determined by the C-sp² surrounding atoms are 1.77(7)°, 3.48(7)°, 4.1(3)° and 3.7(2)° respectively.² Similar deviations were found in 1-thiocarbamoylimidazolidine-2-thione¹⁷, diphenylhydantoin,¹⁸ in the copper(I)

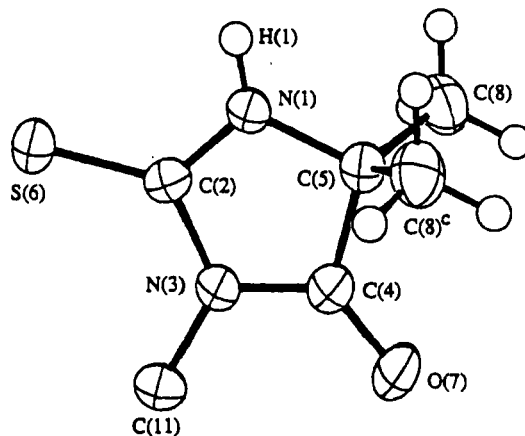


FIGURE 1 ORTEP view of the molecular structure of 3,5,5-trimethyl-4-oxoimidazolidine-2-thione. Thermal ellipsoids are drawn at the 30% probability level.

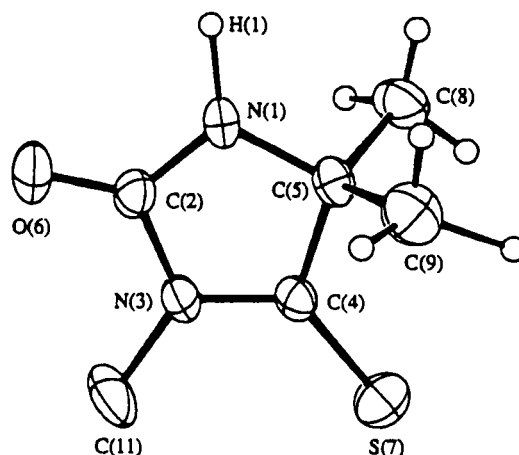


FIGURE 2 ORTEP view of the molecular structure of 3,5,5-trimethyl-4-thioxoimidazolidine-2-one. Thermal ellipsoids are drawn at the 30% probability level.

complexes of (4) and 5,5-dimethyl-4-thioxoimidazolidine-2-one¹⁹ and in several mercury(II) complexes of 5,5-dimethyl-4-oxoimidazolidine-2-thione.⁵⁻⁷ The analysis of the molecular packing shows that in both structures the molecules are bonded by hydrogen bonds realized through the oxygen atom (Table 4).

Bond distances and angles for (1) and (2) are quoted in Table 4. Comparing the results obtained for (1) with those found by us²⁰ on 2-thiohydantoin, it can be seen that the methyl groups do not affect the thiohydantoin skeleton, whose bond distances and angles are not significantly different in the two structures. From the comparison of the bond distances and angles for (1) and (2), one can note that i) the C(2)-N(3) bond undergoes a lengthening of 0.029 Å on passing from (1) to (2); ii) at the same time the N(3)-C(4) bond is shortened by 0.017 Å; iii) the C=S bond distance is shortened by 0.020 Å in (2) and is thus the shortest C=S bond between all other studied pentaatomic rings and very close to a double bond. However, the C=S bond distances in the present molecules are very close to the distances found in the previously reported structures^{2,6,7,19} and they are considerably lower than 1.708 Å, which is the C=S bond distance found in ethylenethiourea²¹ (etu). This length agrees well with the high contribution of the zwitterionic forms of etu, evaluated by Wheatley²¹ at about 80% and by the HOSE model²²⁻²³ at 80.4%. The HOSE (Simple-Harmonic-Oscillator Calculations) model²²⁻²³ uses the crystallographic bond lengths and force constants²⁴ in determining the contribution to the resonance of all the possible canonical structures. The results of the calculation for (1), (2) together with those of the previously reported 2-thiohydantoin² are collected in the Scheme as resonance structure contributions Ci(%). The presence of the three methyl groups in (1) induces very little changes on Ci as compared to 2-thiohydantoin. By summing the Ci contributions of all the structures containing X⁻ and Y⁻, it can be seen that X⁻ [86% and 66% for (1) and (2) respectively] is more nucleophilic than Y⁻ [44% and 57% for (1) and (2) respectively]. This agrees well with the results obtained in the reaction with molecular diiodine^{13,25}; in fact, among the adducts obtained between molecular diiodine and all the studied thiohydantoin, (2) shows the lowest stability constant.¹³

TABLE I
 Crystallographic data

COMPOUND	1	2
FORMULA	C ₈ H ₁₀ N ₂ OS	C ₈ H ₁₀ N ₂ OS
F.w. (amu)	158.22	158.22
Crystal system	orthorhombic	orthorhombic
Space Group	Pnma	Pbca
a (Å)	11.310(10)	8.349(4)
b (Å)	7.326(2)	9.719(8)
c (Å)	10.675(6)	20.337(11)
U (Å ³)	884(1)	1650(3)
Z	4	8
D calc'd (gcm ⁻³)	1.188	1.274
μ(Mo-Kα) (cm ⁻¹)	2.94	3.15
Scan mode	ω	ω
ω-scan width (°)	1.8+0.35tanθ	2.1+0.35tanθ
θ-range (°)	3 - 25	3 - 25
octants of reciprocal space explored	±h, +k, +l	+h, +k, +l
measured reflections	1495	1564
unique observed reflections with I>2σ(I)	415	540
Final R and Rw indices *	0.033, 0.039	0.038, 0.043
No. of variables	87	131
ESD *	0.881	1.175

* $R = [\sum (F_o - k|F_c|) / \sum F_o]$ $R_w = [\sum w(F_o - k|F_c|)^2 / \sum wF_o^2]^{1/2}$
 & $ESD = [\sum w(F_o - k|F_c|)^2 / (N_{\text{observations}} - N_{\text{variables}})]^{1/2}$

The HOSE calculation agrees well with the ¹³C NMR chemical shifts reported in Table 5. In fact, the high value of the chemical shift (210.34 ppm) for C(4) in (2) corresponds to a high contribution (29.5%) of the resonating structures with a positive charge on C(4). In Table 5, the ¹³C NMR chemical shifts of 3,5,5-trimethylimidazolidine-2,4-dione (8) and 3,5,5-trimethylimidazolidine-2,4-dithione (9) are also reported for comparison. The chemical shifts of C(2) in (8) and (2) undergo high deshieldings with the substitution of oxygen with sulphur [(1) and (9)], leaving the chemical shifts of C(4) practically unchanged; deshieldings of the

TABLE II
Positional parameters and their estimated standard deviations
for compound (1)

Atom	x	y	z
S(6)	0.3634(1)	0.250	0.04995(9)
O(7)	0.7574(2)	0.250	-0.1550(3)
N(1)	0.4511(3)	0.250	-0.1826(3)
N(3)	0.5876(3)	0.250	-0.0381(3)
C(2)	0.4671(3)	0.250	-0.0588(3)
C(4)	0.6493(4)	0.250	-0.1474(3)
C(5)	0.5608(4)	0.250	-0.2533(4)
C(8)	0.5718(3)	0.0774(5)	-0.3336(3)
C(11)	0.6435(4)	0.250	0.0842(3)
H(1)	0.378(3)	0.250	-0.215(3)
H(81)	0.574(3)	-0.026(4)	-0.286(2)
H(82)	0.644(3)	0.081(4)	-0.382(2)
H(83)	0.500(3)	0.071(5)	-0.385(3)
H(111)	0.610(3)	0.139(6)	0.132(3)
H(112)	0.699(4)	0.159(5)	0.093(3)
H(113)	0.733(4)	0.250	0.061(4)
H(114)	0.582(5)	0.250	0.144(4)

same entity are verified in the substitution of oxygen with sulphur on C(4) [compare (8) and (1) with (2) and (9)]. The substitution of oxygen with sulphur produces deshieldings also on C(5), C(8)-C(9) and C(11), all explainable in terms of the closeness of each carbon to the substitution position.

In Table 6, the structural parameters around the C(sp²) are collected together with those reported for other hydantoin derivatives.² As can be seen from the values of (β - γ), the C=X is almost symmetrical with respect to the nitrogens only in (1); in all the other molecules, the β angles are always greater than γ , in consequence of the higher conjugation of the lone-pair of N(1) with respect to N(3), which promotes a higher repulsion of this bond with CX (VSEPR model).²⁶ The VSEPR model has been employed successfully to explain the changes in the angles in 5,5-dimethylimidazolidine-2,4-dithione and 5,5-dimethylimidazolidine-2-one-4-thione under complexation with copper(I).¹⁹ On the other hand, the N(1)-C(2), C(2)-N(3) and N(3)-C(4) bonds, which are affected by the π -electron charge distribution, show different lengths according to the conjugation of the nitrogen

TABLE III
Positional parameters and their estimated standard deviations
for compound (2)

Atom	x	y	z
S(7)	0.1938(2)	0.0684(1)	0.20134(7)
O(6)	0.2758(4)	-0.2511(4)	0.0141(2)
N(1)	0.0447(5)	-0.1873(4)	0.0672(2)
N(3)	0.2712(4)	-0.1020(4)	0.1036(2)
C(2)	0.2018(6)	-0.1888(4)	0.0560(2)
C(4)	0.1615(5)	-0.0424(4)	0.1426(2)
C(5)	-0.0007(5)	-0.0958(4)	0.1217(2)
C(8)	-0.1090(6)	0.0190(5)	0.0981(3)
C(9)	-0.0784(6)	-0.1793(5)	0.1765(3)
C(11)	0.4444(6)	-0.0796(5)	0.1080(3)
H(1)	-0.035(5)	-0.229(4)	0.041(2)
H(81)	-0.049(6)	0.069(4)	0.068(2)
H(82)	-0.130(4)	0.068(4)	0.137(2)
H(83)	-0.215(6)	-0.018(5)	0.081(2)
H(91)	-0.179(6)	-0.232(6)	0.159(2)
H(92)	-0.010(5)	-0.257(5)	0.189(2)
H(93)	-0.116(5)	-0.117(5)	0.209(2)
H(111)	0.489(8)	-0.099(6)	0.074(3)
H(112)	0.463(6)	0.011(5)	0.113(2)
H(113)	0.493(9)	-0.147(7)	0.135(3)

lone pairs under the influence of the exo-chalcogen atoms. For all the studied compounds² (see Table 4), the CN length increases in the order N(1)-C(2) < N(3)-C(4) < C(2)-N(3), since the lone pair of N(1) moves towards the C(2), whereas that of N(3) moves predominantly towards the C(4).

EXPERIMENTAL

Compound preparation. The previously reported^{13,14} syntheses of 3,5,5-trimethyl-4-oxoimidazolidine-2-thione (1) and 3,5,5-trimethyl-4-thioxoimidazolidin-2-one (2) have been improved according to the following procedures.

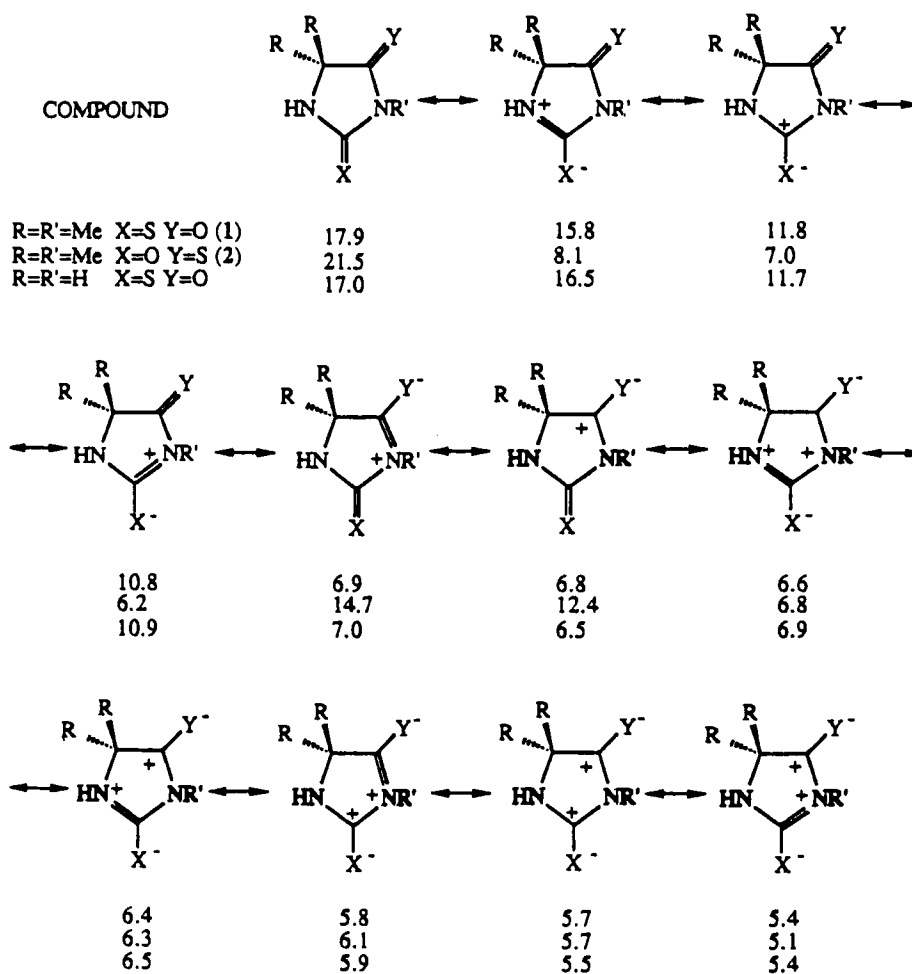
3,5,5-Trimethyl-4-oxoimidazolidine-2-thione (1). A mixture of 3,5,5-trimethyl-2,4-dithioxoimidazolidine (0.8 g, 4.6 mmol), HgO (1 g, 4.6 mmol) and 5% HCl (40 ml) was refluxed for 24 h. It was then

TABLE IV
Bond distances (Å), angles (°) and hydrogen bonds

	1	2
N(1)–C(2)	1.334(5)	1.332(6)
C(2)–N(3)	1.380(6)	1.409(5)
N(3)–C(4)	1.360(6)	1.343(5)
C(4)–C(5)	1.510(7)	1.511(6)
C(5)–N(1)	1.453(6)	1.471(5)
C(5)–C(8)	1.533(5)	1.514(7)
C(5)–C(9)		1.523(7)
N(3)–C(11)	1.451(6)	1.465(7)
C(2)–S(6)	1.650(5)	
C(2)–O(6)		1.214(5)
C(4)–O(7)	1.225(6)	
C(4)–S(7)		1.630(4)
N(1)–H(1)	0.89(4)	0.95(5)
O(7)...H(1) ^a	1.95(4)	
O(7)...N(1) ^a	2.794(5)	
O(6)...H(1) ^b		1.94(5)
O(6)...N(1) ^b		2.852(5)
N(1)–C(2)–N(3)	107.0(4)	106.3(4)
C(2)–N(3)–C(4)	111.6(4)	112.6(4)
N(3)–C(4)–C(5)	107.6(5)	107.2(3)
C(4)–C(5)–N(1)	100.2(4)	100.9(4)
C(5)–N(1)–C(2)	113.5(4)	112.9(4)
C(2)–N(3)–C(11)	125.1(4)	122.4(5)
C(4)–N(3)–C(11)	123.3(4)	125.0(5)
N(1)–C(2)–S(6)	126.9(3)	
N(1)–C(2)–O(6)		128.8(5)
N(3)–C(2)–S(6)	126.1(4)	
N(3)–C(2)–O(6)		124.9(4)
N(3)–C(4)–O(7)	124.6(5)	
N(3)–C(4)–S(7)		127.2(3)
C(5)–C(4)–O(7)	127.7(4)	
C(5)–C(4)–S(7)		125.5(3)
N(1)–C(5)–C(8)	111.1(3)	111.1(5)
N(1)–C(5)–C(9)		109.8(4)
C(4)–C(5)–C(8)	111.4(3)	111.8(4)
C(4)–C(5)–C(9)		111.0(4)
C(8)–C(5)–C(8) ^c	111.2(5)	
C(8)–C(5)–C(9)		111.7(5)
O(7)...H(1) ^a –N(1) ^a	158(4)	
O(6)...H(1) ^b –N(1) ^b		160(4)
Symmetry codes: a=1/2+x, 1/2–y, –1/2–z; b=1/2+x, –y–1/2, –z;		
c=x, 1/2–y, z.		

filtered to eliminate HgS and the filtrate was extracted with CHCl₃. The organic extract was washed with water, dried and concentrated under reduced pressure. The residue was purified by flash-chromatography on silica gel, using a mixture of CHCl₃ and THF (in a v/v 95:5 ratio, respectively) as eluant, to give (1) (0.32 g, 44% yield). This compound, which was homogeneous to TLC analyses, had m.p. 141–142°C (from CHCl₃) (lit.¹³ 135–137°C). ¹³C-NMR (solvent CDCl₃): δ 23.95, 27.33, 60.37, 182.72, 177.06 ppm. IR (KBr): ν 3230(s), 3009(w), 2981(w), 2945(w), 1727(s), 1518(s), 1475(m), 1443(m), 1397(m), 1314(s), 1231(w), 1203(m), 1110(s), 1058(s), 981(m), 927(m), 838(m), 754(w), 719(s), 646(m), 604(w), 571(m), 494(m), 437(w), 357(m), 320(m) cm^{–1}. IR (CHCl₃ in the 3500–3000 cm^{–1} and 1800–1600 cm^{–1} ranges): ν 3446(m), 3202(wbr), 1746(s) cm^{–1}. UV (CH₂Cl₂, 7.3.10^{–5} mol/l): λ_{max} (ε), 266(15700), 304(4300) nm.

Resonance Structure Contributions Ci (%) evaluated by the HOSE Model.

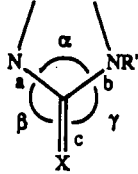


SCHEME

TABLE V
 ^{13}C NMR Chemical Shifts for (1), (2), 3,5,5-trimethylimidazolidine-2,4-dione (8)
 and 3,5,5-trimethylimidazolidine-2,4-dithione (9)

Compound	C(2)	C(4)	C(5)	C(8)-C(9)	C(11)
(8)	157.01	177.59	58.81	24.84	24.49
(1)	182.72	177.06	60.37	23.95	27.33
(2)	156.72	210.34	67.01	28.65	29.28
(9)	181.39	209.37	71.35	27.97	32.35

TABLE VI
Bond lengths (Å) and angles (°) around C(2) in several hydantoin derivatives



Compound	X	R'	α	β	γ	$\beta-\gamma$	a	b	c	Ref.
(1)	S	Me	107.0	126.9	126.1	0.8	1.334	1.380	1.650	this work
(2)	O	Me	106.3	128.8	124.9	3.9	1.332	1.409	1.214	this work
(3)	S	H	106.8	128.4	124.7	3.7	1.325	1.378	1.648	1
(4)	S	H	105.7	130.0	124.3	5.7	1.326	1.339	1.648	1
(5)	Se	H	108.0	128.2	123.7	4.5	1.32	1.36	1.805	1
(6)	S	H	107.0	129.6	123.4	6.2	1.308	1.386	1.668	1
(7)	SMe	H	115.5	128.2	116.3	11.9	1.280	1.385	1.741	2

(3) 2-thiohydantoin; (4) 5,5-dimethylimidazolidine-2,4-dithione; (5) 5,5-dimethyl-2-selenoxoimidazolidin-4-one; (6) 5,5-dimethyl-4-selenoxoimidazolidine-2-thione; (7) Δ^1 -2-S-methyl-5,5-dimethylimidazolidin-4-one.

3,5,5-Trimethyl-4-thioxoimidazolidine-2-one (2). A mixture of 3,5,5-trimethylimidazolidine-2,4-dione (3.75 g, 26 mmol), P_2S_5 (2.89 g, 13 mmol) and dioxane (50 ml) was refluxed for 1 h. It was then filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by flash-chromatography on silica gel, using a mixture of $CHCl_3$ and THF (in a v/v 95:5 ratio, respectively) as eluant, to give (2) (1.22 g, 30% yield). This compound, which was homogeneous to TLC analyses, had: m.p. 125–126°C (from benzene). ^{13}C -NMR (solvent $CDCl_3$): δ 28.65, 29.28, 67.01, 156.72, 210.34 ppm. IR (KBr): ν 3284(s), 2988(w), 2938(w), 1761(s), 1714(s), 1468(m), 1390(m), 1375(m), 1325(s), 1211(w), 1174(w), 1142(s), 1033(m), 986(m), 923(m), 870(w), 758(m), 685(m), 665(m), 631(s), 595(m), 490(s), 446(w), 357(m), 330(w) cm^{-1} . IR ($CHCl_3$ in the 3500–3000 cm^{-1} and 1800–1600 cm^{-1} ranges): ν 3455(m), 3251(wbr), 1755(s) cm^{-1} . UV (CH_2Cl_2 , $6.9 \cdot 10^{-5}$ mol/l): λ_{max} (ϵ), 276(16800) nm. Elem. Anal.: (calc.d% for $C_6H_{10}N_2OS$) found %: C (45.6) 45.8, H (6.3) 6.5, N (17.7) 18.0, S (20.3) 20.6.

Spectroscopic measurements. ^{13}C -NMR were recorded on a Varian VXR 300 MHz spectrometer using TMS as internal standard. UV spectra were recorded using an HP 8452A Diode Array Spectrophotometer, connected with HP Vectra 286/12 PPC. The i.r. spectra (3500–3050 cm^{-1} and 1800–1600 cm^{-1}) were recorded in $CHCl_3$ solutions using a Perkin-Elmer 983 instrument connected with a Perkin-Elmer 7500 data station. The i.r. spectra (3500–200 cm^{-1}) on the solid samples were recorded as KBr disc.

X-Ray data collection and structure determination. Crystal data for compounds (1) and (2) and other experimental details are summarized in Table 1. The diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature, using $Mo-K\alpha$ radiation ($\lambda = 0.71073$ Å). All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.¹⁵ The diffracted intensities were corrected for Lorentz-polarization but not for absorption. Scattering factors and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from Ref. 16. Both structures were solved by direct methods (MULTAN), and refined

by full-matrix least-squares, minimizing the function $\sum w(F_o - k|F_c|)^2$. Weights assigned to individual observations were in the form: $1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (iI)^2]^{1/2}/2F_oL_p$, with $i = 0.07$ and 0.05 for compound (1) and (2) respectively. Anisotropic thermal factors were refined for all the nonhydrogen atoms, and isotropic factors for the hydrogen atoms. For compound (1) the presence of a crystallographic symmetry mirror for the molecule leads to a disordered situation for the methyl C(11) lying on the plane so that the hydrogen atoms attached to C(11) appear splitted into two staggered conformations. The final difference Fourier synthesis showed residuals less than $0.2 \text{ e}/\text{\AA}^2$ for both compounds. The fractional atomic coordinates for compounds (1) and (2) are listed in Tables 2 and 3 respectively.

Anisotropic thermal parameters and structure factor moduli have been deposited [4 pages for (1) and 5 pages for (2)].

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