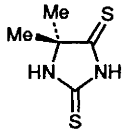
An X-Ray, Spectroscopic and Semiempirical Quantum-mechanical Study on Complexes of Thiones and Selones with Molecular Diiodine[†]

Franco Cristiani,[a] Francesco Demartin,[b] Francesco A. Devillanova,[*,a] Franceso Isaia,[a] Giuseppe Saba[c] and Gaetano Verani[a]
[a] *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Via Ospedale 72, 09124 Cagliari, Italy*
[b] *Istituto di Chimica Strutturistica Inorganica e Centro CNR, via G. Venezian 21, 20133 Milano, Italy*
[c] *Dipartimento di Scienze Chimiche, Via Ospedale 72, 09124 Cagliari, Italy*

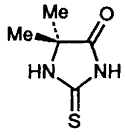
The crystal structures of four neutral charge-transfer molecular compounds formed between 5,5-dimethylimidazolidine-2,4-dithione **1**, 5,5-dimethyl-2-thioxoimidazolidin-4-one **2** and 5,5-dimethyl-2-selenoxoimidazolin-4-one **3** and molecular diiodine have been determined. While all donors form 1 : 1 complexes, **1** also gives a 1 : 2 adduct when crystallized from a solution containing an excess of molecular diiodine. The compound **1**·I_2 is monoclinic [a = 6.681(1), b = 22.212(4), c = 7.854(1) Å, β = 98.89(1)°, Z = 4, space group $P2_1/n$; R = 0.024] and consists of discrete moieties of the molecular formula with molecular diiodine bonded to the sulfur at C(2). The compound **1**·$2I_2$ is monoclinic [a = 14.757(2), b = 6.136(1), c = 16.284(3) Å, β = 96.33(1)°, Z = 4, space group $P2_1/c$; R = 0.028] and consists of discrete moieties of the molecular formula with the two molecules of diiodine bonded to the two sulfur atoms. An extended network of interactions between the iodine atoms determines the crystal packing. Also **2**·I_2 is monoclinic [a = 13.183(3), b = 6.106(1), c = 14.550(2) Å, β = 113.29(1)°, Z = 4, space group $P2_1/n$; R = 0.024] and consists of discrete moieties of the molecular formula with the molecular diiodine bonded to the sulfur at C(2). The compound **3**·I_2 is triclinic [a = 8.034(3), b = 8.769(4), c = 9.805(5) Å, α = 63.44(1), β = 67.56(4), γ = 67.01(4)°, Z = 2, space group $P\bar{1}$; R = 0.038] and contains discrete moieties of the molecular formula with the diiodine strongly bonded to the selenium atom. In all the structures the diiodine is almost coplanar with the ring plane. Quantum-mechanical calculations (PM3) have been carried out on **1**·I_2 and **2**·I_2 in order to clarify the discrepancy between the S ··· I bond distances in the two structures and the corresponding interaction in CH_2Cl_2 solution, measured as spectrophotometric stability constants. The Fourier-transform Raman frequencies of ν(I–I) are correlated with the lengthening of the I–I bond distances. The ^{13}C NMR chemical shifts of the 1 : 1 complexes for the two sulfur derivatives are also reported.

Diiodine (I_2) forms molecular charge-transfer (c.t.) complexes with a variety of molecules containing heteroatoms such as nitrogen, oxygen, sulfur or selenium. In previous papers[1] we have investigated the interaction between diiodine and several series of pentaatomic rings, all containing thio- or seleno-amido groups as donors (D) by ultraviolet–visible spectroscopy. 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 (K) and the thermodynamic parameters of the 1:1 adduct of the reaction $D + I_2 \rightleftharpoons D\cdot I_2$. This type of research was first stimulated by interest in the molecular compounds formed between antithyroid drugs and diiodine in studies on hyperthyroidism.[2] More recently, the sulfur–iodine charge-transfer complexes have been shown to possess promising electrical properties.[3–5] This has led us to prepare and study sulfur- and selenium–iodine complexes in the solid state.

In this paper we report the crystal structures of the adducts obtained by treating molecular diiodine with 5,5-dimethylimidazolidine-2,4-dithione **1**, 5,5-dimethyl-2-thioxoimidazolidin-4-one **2** and 5,5-dimethyl-2-selenoxoimidazolidin-4-one **3**. The crystal data are discussed in comparison with the results of a PM3 semiempirical calculation carried out on **1**·I_2 and **2**·I_2 and with the Fourier-transform Raman frequencies of the ν(I–I) vibrations; furthermore, the ^{13}C NMR chemical shifts of the 1 : 1 c.t. complexes of **1** and **2** and the method used for their calculation are reported.



1



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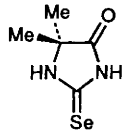

3

Experimental

Compound Preparation.—Compounds **1**–**3** were prepared and purified according to the literature.[6–8] The 1 : 1 molecular complexes were prepared by dissolving the appropriate donor in dichloromethane and then adding the stoichiometric amount of I_2 dissolved in dichloromethane. For the 1:2 complex of 5,5-dimethylimidazolidine-2,4-dithione, an excess of I_2 with respect to the stoichiometric amount was used. In all cases, very slow evaporation of the solvent yields crystalline products, suitable for X-ray analysis. All crystals were deep red (Found: C, 14.3; H, 2.1; N, 6.9; S, 15.3. Calc. for $C_5H_8I_2N_2S_2$ **1**·I_2: C, 14.5; H, 1.9; N, 6.7; S, 15.4. Found: C, 8.8; H, 1.1; N, 3.9; S, 9.8. Calc. for

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: cal = 4.184 J.

Table 1 Crystallographic data

Compound	$1{\cdot}I_2$	$1{\cdot}2I_2$	$2{\cdot}I_2$	$3{\cdot}I_2$
Formula	$C_5H_8I_2N_2S_2$	$C_5H_8I_4N_2S_2$	$C_5H_8I_2N_2OS$	$C_5H_8I_2N_2OSe$
M	414.07	667.88	398.00	444.90
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	6.681(1)	14.757(2)	13.183(3)	8.034(3)
b/Å	22.212(4)	6.136(1)	6.106(1)	8.769(4)
c/Å	7.854(1)	16.284(3)	14.550(2)	9.805(5)
α/°	90	90	90	63.44(1)
β/°	98.89(1)	96.33(1)	113.29(1)	67.56(4)
γ/°	90	90	90	67.01(4)
U/Å^3	1151.5(6)	1465.5(7)	1075.8(6)	550.5(3)
Z	4	4	4	2
$F(000)$	760	1184	728	400
D_c/g cm^{-3}	2.388	3.027	2.457	2.684
μ(Mo-Kα)/cm^{-1}	57.07	86.62	59.29	88.85
Crystal dimensions (mm)	0.12 × 0.15 × 0.25	0.10 × 0.18 × 0.27	0.08 × 0.16 × 0.30	0.12 × 0.13 × 0.20
Minimum transmission factor	0.75	0.63	0.42	0.68
Scan mode	ω	ω	ω	ω
ω-Scan width/°	$1.1 \pm 0.35\tan\theta$	$1.0 + 0.35\tan\theta$	$1.1 + 0.35\tan\theta$	$1.1 + 0.35\tan\theta$
θ Range/°	3–27	3–25	3–27	3–27
Octants of reciprocal space explored	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, \pm k, \pm l$
Measured reflections	2725	2563	2635	2394
Maximum decay (on F_o) (%)	9	11	28	None
Unique observed reflections with $I > 3\sigma(I)$, N_o	2075	2125	1933	2084
Final R, R' indices[a]	0.024, 0.035	0.028, 0.040	0.024, 0.034	0.038, 0.054
No. of variables, N_v	132	150	133	132
e.s.d.[b]	1.759	1.656	1.418	2.374
Maximum electron density residual/e Å^{-3}	0.7	0.7	0.9	1.1

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. [b] e.s.d. $= [\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

Table 2 Fractional atomic coordinates for the compound $1{\cdot}I_2$

Atom	x	y	z
I(1)	0.131 12(4)	0.154 32(1)	−0.200 67(3)
I(2)	−0.189 27(4)	0.237 45(1)	−0.213 83(4)
S(6)	0.437 4(2)	0.072 12(5)	−0.206 7(1)
S(7)	1.090 0(2)	0.041 86(6)	0.270 4(2)
N(1)	0.569 5(4)	0.119 0(1)	0.110 3(4)
N(3)	0.771 4(4)	0.054 1(1)	0.021 2(4)
C(2)	0.591 0(5)	0.084 1(2)	−0.019 7(4)
C(4)	0.871 3(5)	0.068 4(2)	0.178 9(5)
C(5)	0.741 4(5)	0.113 9(2)	0.254 5(4)
C(8)	0.666 9(6)	0.091 2(2)	0.415 5(5)
C(9)	0.854 0(6)	0.173 9(2)	0.288 0(5)
H(1)	0.479(8)	0.145(2)	0.121(7)
H(3)	0.813(4)	0.031(1)	−0.041(4)
H(81)	0.567(6)	0.116(2)	0.454(5)
H(82)	0.775(6)	0.092(2)	0.503(6)
H(83)	0.611(6)	0.057(2)	0.383(6)
H(91)	0.787(6)	0.202(2)	0.314(5)
H(92)	0.886(7)	0.188(2)	0.190(6)
H(93)	0.987(8)	0.183(3)	0.384(8)

Table 3 Fractional atomic coordinates for the compound $1{\cdot}2I_2$

Atom	x	y	z
I(1)	0.338 67(3)	0.256 74(8)	0.823 25(3)
I(2)	0.462 36(3)	0.614 27(8)	0.841 81(3)
I(3)	0.043 37(3)	−0.803 34(8)	0.595 16(3)
I(4)	−0.060 13(3)	−1.115 32(9)	0.664 58(3)
S(6)	0.215 2(1)	−0.077 1(3)	0.802 5(1)
S(7)	0.160 7(1)	−0.521 1(3)	0.517 4(1)
N(1)	0.306 0(3)	−0.129 6(9)	0.666 8(3)
N(3)	0.181 4(4)	−0.321 7(9)	0.665 1(3)
C(2)	0.237 8(4)	−0.173(1)	0.710 6(4)
C(4)	0.210 5(4)	−0.366(1)	0.591 6(4)
C(5)	0.298 2(4)	−0.244(1)	0.586 7(4)
C(8)	0.378 3(5)	−0.403(1)	0.583 1(5)
C(9)	0.291 3(5)	−0.083(1)	0.516 5(5)
H(1)	0.358(4)	−0.02(1)	0.683(4)
H(3)	0.122(4)	−0.39(1)	0.690(4)
H(81)	0.386(5)	−0.48(1)	0.624(5)
H(82)	0.387(5)	−0.49(1)	0.529(5)
H(83)	0.431(4)	−0.34(1)	0.595(4)
H(91)	0.232(5)	0.02(1)	0.519(5)
H(92)	0.335(5)	−0.02(2)	0.518(6)
H(93)	0.285(5)	−0.16(1)	0.466(5)

$C_5H_8I_4N_2S_2$ $1{\cdot}2I_2$: C, 8.9; H, 1.2; N, 4.1; S, 9.6. Found: C, 14.9; H, 1.9; N, 6.9; S, 8.3. Calc. for $C_5H_8I_2N_2OS$ $2{\cdot}I_2$: C, 15.1; H, 2.0; N, 7.0; S, 8.1. Found: C, 13.3; H, 2.1; N, 6.1. Calc. for $C_5H_8I_2N_2OSe$ $3{\cdot}I_2$: C, 13.5; H, 2.0; N, 6.3%).

X-Ray Data Collection and Determination of Structures.—The diffraction measurements were carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystals of the compounds were coated with cyanoacrylate glue in order to prevent decomposition during data collection due to loss of diiodine. This expedient allowed better results than simply sealing the crystals in a capillary glass. Nevertheless, in some cases, a small decay of the crystal was observed. The diffracted intensities were corrected for Lorentz, polarization, absorption (empirical correction),[9] and decay, but not for extinction. Scattering factors for all the atomic species and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref. 10. The structure, in all cases, was solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{\frac{1}{2}}/2F_oL_p$, $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics and k (=0.04) is a coefficient for improving the goodness of fit.

An anisotropic thermal parameter was assigned to all the non-

Table 4 Fractional atomic coordinates for the compound **2**·I_2

Atom	*x*	*y*	*z*
I(1)	0.216 81(2)	0.133 81(5)	0.052 87(1)
I(2)	0.138 88(3)	−0.214 04(5)	0.132 48(2)
S(6)	0.288 62(7)	0.463 3(2)	−0.038 16(6)
O(7)	0.582 2(3)	1.000 1(5)	0.138 1(2)
N(1)	0.427 8(2)	0.549 8(5)	0.153 2(2)
N(3)	0.447 2(2)	0.762 0(6)	0.041 1(2)
C(2)	0.388 9(2)	0.589 7(6)	0.056 4(2)
C(4)	0.524 1(3)	0.841 4(8)	0.129 6(2)
C(5)	0.519 0(3)	0.697 4(6)	0.212 4(2)
C(8)	0.626 2(3)	0.571 4(8)	0.262 8(3)
C(9)	0.489 9(3)	0.829 3(8)	0.287 8(3)
H(1)	0.392(3)	0.434(8)	0.174(3)
H(3)	0.434(3)	0.788(7)	−0.017(3)
H(81)	0.623(3)	0.481(7)	0.321(3)
H(82)	0.653(3)	0.503(7)	0.227(3)
H(83)	0.694(2)	0.667(6)	0.293(2)
H(91)	0.502(4)	0.73(1)	0.352(3)
H(92)	0.545(3)	0.950(8)	0.316(3)
H(93)	0.413(4)	0.882(8)	0.249(3)

Table 5 Fractional atomic coordinates for the compound **3**·I_2

Atom	*x*	*y*	*z*
I(1)	0.355 37(4)	0.333 83(4)	0.536 50(3)
I(2)	0.212 07(5)	0.675 66(5)	0.301 39(4)
Se(6)	0.520 75(7)	0.032 07(7)	0.739 22(7)
O(7)	0.281 1(5)	−0.514 5(4)	0.980 1(5)
N(1)	0.207 7(5)	−0.064 5(5)	0.757 8(5)
N(3)	0.411 9(5)	−0.282 5(5)	0.876 0(5)
C(2)	0.366 6(6)	−0.108 4(6)	0.790 6(5)
C(4)	0.275 6(6)	−0.360 4(6)	0.905 5(6)
C(5)	0.124 0(6)	−0.214 6(6)	0.831 1(5)
C(8)	0.086 3(7)	−0.251 9(7)	0.708 3(6)
C(9)	−0.054 4(7)	−0.185 2(6)	0.960 7(6)
H(1)	0.12(1)	0.05(1)	0.708(8)
H(3)	0.490(8)	−0.333(7)	0.916(6)
H(81)	0.182(8)	−0.248(7)	0.622(6)
H(82)	0.078(8)	−0.382(8)	0.751(6)
H(83)	0.003(8)	−0.163(7)	0.640(6)
H(91)	−0.01(1)	−0.170(9)	1.034(7)
H(92)	−0.142(8)	−0.089(8)	0.907(6)
H(93)	−0.097(6)	−0.270(5)	1.004(5)

hydrogen atoms. All the hydrogen atoms were located in Fourier difference maps and their positions and thermal parameters refined. The crystallographic data for the four structures are reported in Table 1 and fractional atomic coordinates for **1**·I_2, **1**·2I_2, **2**·I_2 and **3**·I_2 are in Tables 2–5.

All calculations were performed on a PDP 11/73 computer using the SDP-Plus Structure Determination Package.[11] Bond distances and angles are reported in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

^{13}C *NMR Chemical Shift Determination of the* 1:1 *Complexes*.—The ^{13}C NMR spectra were recorded on a Varian FT VXR 300 spectrometer, operating at 75.4 MHz, in CH_2Cl_2 solution at 20 °C and referred to $CDCl_3$ (δ 77.00) as external standard. In order to determine the chemical shifts of the 1:1 complexes for the thione compounds, the spectra were recorded of several solutions of the two reagents with increasing amounts of diiodine. Since the experimental design in the NMR measurements cannot be as good as that obtained for UV/VIS data, we optimized only the chemical shifts of the 1:1 complexes using spectrophotometric formation constants.[1e]

The attribution of the signals of carbons C(2) and C(4) in compound **1** required the preparation of the [$^2H_6$] compound **1′**. By comparing the ^{13}C H-decoupled spectra of **1** and **1′** it was possible to assign the peak at δ 179.27 to C(2) and that at δ 210.31 to C(4). Only the latter signal shows an apparently broader peak due to ^3J(C–D) coupling between C(4) and the deuterium atoms of the CD_3 groups.

Fourier-transform Raman Spectra.—These spectra were recorded on an FRA 106 FT Raman accessory mounted on a Bruker IFS 66 FT-IR vacuum instrument, operating with an exciting frequency of 1064 nm (Nd YAG laser). The samples were stable to the laser beam.

Semiempirical Calculations.—The equilibrium geometries were calculated at a semiempirical quantum-mechanical level using the PM3 Hamiltonian as implemented in the MOPAC package.[12] The geometries obtained in the first optimization run were subsequently refined using a much lower gradient threshold ($g < 0.01$ kcal Å^{-1} mol^{-1}).

Results

5,5-*Dimethylimidazolidine*-2,4-*dithione–Diiodine* (1/1).—The **1**·I_2 moieties form discrete units [Fig. 1(*a*)] in the crystal and the contacts among the different units are normal van der Waals interactions. The imidazolidine ring is planar, the maximum deviation from the mean plane [0.004(3) Å] being due to N(1). The atoms S(6) and S(7) are out of the ring plane by −0.050(1) and 0.010(1) Å respectively. The linear S···I–I fragment is practically in the plane of the organic molecule. The dihedral angle between the plane defined by N(1), C(2), S(6) and I(1) and the mean plane of the imidazolidine ring is 4.1°.

5,5-*Dimethylimidazolidine*-2,4-*dithione–Diiodine* (1/2).—The **1**·2I_2 moieties form discrete units [Fig. 1(*b*)] in the crystal; the crystal packing of these moieties determines a wide network of diiodine molecules (Fig. 2), in which each diiodine interacts with the others with contacts sometimes shorter than the normal van der Waals distance (4.2–4.3 Å).[4] The imidazolidine ring is essentially planar, the deviations from the mean plane for C(2), N(3) and C(4) being respectively 0.011(7), −0.015(6) and 0.012(6) Å; atoms S(6) and S(7) are out of the ring plane by 0.069(2) and 0.085(2) Å. The planes around the sp^2 carbons, defined by N(1), C(2), N(3) and S(6) and by N(3), C(4), C(5) and S(7), are strictly planar and form a dihedral angle of 4.0°, while the corresponding dihedral angle in **1**·I_2 is 1.1°.

Also in this structure, the S···I–I fragment is practically linear (Table 6) for S(6)···I(1)–I(2) [177.94(4)°], but forms an angle of 173.74(4)° for S(7)···I(3)–I(4). The mean planes, defined by N(1), C(2), S(6) and I(1) and by N(3), C(4), S(7) and I(3), form dihedral angles of 11.5 and 17.6° with the ring plane, indicating that the iodine atoms tend to be displaced off the imidazolidine plane.

5,5-*Dimethyl*-2-*thioxoimidazolidin*-4-*one–Diiodine* (1/1).—The contacts between the **2**·I_2 units are the normal van der Waals interactions between the iodine atoms and the hydrogen bonding O(7)···H(3)–N(3) (Table 6). The imidazolidine ring is roughly planar, with the thioketone sulfur in the plane, but O(7) is off this plane by −0.086(4) Å. Also in this adduct the planes around the sp^2 carbons are strictly planar and form a dihedral angle of 3.1°, while the mean plane defined by N(1), C(2), S(6) and I(1) forms a dihedral angle of 0.5° with the ring plane, indicating that the diiodine lies in the molecular plane. The S···I–I fragment is practically linear [Fig. 1(*c*)].

5,5-*Dimethyl*-2-*selenoxoimidazolidin*-4-*one–Diiodine* (1/1).—The **3**·I_2 moieties form discrete units [Fig. 1(*d*)] in the crystal and the contacts between the different units are the normal van der Waals interactions between the iodine atoms. The imidazolidine ring is roughly planar, with the selenium atom −0.093 Å out of the plane. The planes around the sp^2 carbons are strictly planar and form a dihedral angle of 2.4° with respect to each

Table 6 Interatomic distances (Å) and angles (°)

	1·I$_2$	**1**·2I$_2$	**2**·I$_2$	**3**·I$_2$
I(1)–I(2)	2.817(1)	2.849(1)	2.802(1)	2.962(1)
I(3)–I(4)		2.767(1)		
N(1)–C(2)	1.307(4)	1.323(6)	1.317(3)	1.304(4)
C(2)–N(3)	1.372(3)	1.392(7)	1.372(4)	1.349(4)
N(3)–C(4)	1.351(4)	1.343(7)	1.375(4)	1.384(4)
C(4)–C(5)	1.512(4)	1.506(7)	1.514(4)	1.509(4)
C(5)–N(1)	1.487(3)	1.474(6)	1.477(4)	1.476(4)
C(5)–C(8)	1.515(4)	1.537(8)	1.519(5)	1.535(5)
C(5)–C(9)	1.534(4)	1.506(9)	1.527(4)	1.533(5)
C(2)–S(6)	1.678(3)	1.676(5)	1.673(3)	
C(2)–Se(6)				1.861(4)
C(4)–O(7)			1.211(4)	1.207(4)
C(4)–S(7)	1.636(3)	1.645(5)		
I(1)···S(6)	2.748(1)	2.737(1)	2.773(1)	
I(3)···S(7)		2.844(1)		
I(1)···Se(6)				2.699(1)
O(7)···H(3)			2.13(5)$^{\mathrm{I}}$	
O(7)···N(3)			2.874(4)$^{\mathrm{I}}$	
S(7)···H(3)	2.58(3)$^{\mathrm{II}}$			
S(7)···N(3)	3.361(3)$^{\mathrm{II}}$			
I(1)···I(1)				4.070(1)$^{\mathrm{XIII}}$
I(1)···I(2)	4.519(1)$^{\mathrm{III}}$	4.284(1)$^{\mathrm{XV}}$	4.307(1)$^{\mathrm{VII}}$	
I(1)···I(2)	4.917(1)$^{\mathrm{IV}}$	4.341(1)$^{\mathrm{XVI}}$	4.381(1)$^{\mathrm{VIII}}$	4.238(1)$^{\mathrm{XIV}}$
I(1)···I(2)	4.996(1)$^{\mathrm{V}}$		4.416(1)$^{\mathrm{IX}}$	4.299(1)$^{\mathrm{XIII}}$
I(1)···I(4)		4.211(1)$^{\mathrm{XVII}}$		
I(2)···I(2)	4.779(1)$^{\mathrm{VI}}$	4.508(1)$^{\mathrm{XVIII}}$	4.656(1)$^{\mathrm{XII}}$	4.859(1)$^{\mathrm{XIV}}$
I(2)···I(2)		5.337(1)$^{\mathrm{XIX}}$	4.893(1)$^{\mathrm{IX}}$	
I(3)···I(3)		4.024(1)$^{\mathrm{XX}}$		
I(3)···I(3)		4.922(1)$^{\mathrm{XI}}$		
I(3)···I(4)		4.060(1)$^{\mathrm{X}}$		
I(3)···I(4)		4.293(1)$^{\mathrm{XX}}$		
I(3)···I(4)		4.671(1)$^{\mathrm{VIII}}$		
I(4)···I(4)		4.383(1)$^{\mathrm{X}}$		
N(1)–C(2)–N(3)	107.7(2)	106.9(4)	108.0(3)	109.8(3)
C(2)–N(3)–C(4)	113.0(2)	112.2(4)	111.8(3)	111.3(3)
N(3)–C(4)–C(5)	106.6(2)	107.8(4)	107.0(3)	106.3(3)
C(4)–C(5)–N(1)	100.0(2)	100.0(4)	99.9(2)	100.5(3)
C(5)–N(1)–C(2)	112.6(2)	113.0(4)	113.2(3)	112.0(3)
N(1)–C(2)–S(6)	130.7(2)	130.4(4)	129.9(2)	
N(1)–C(2)–Se(6)				129.5(3)
N(3)–C(2)–S(6)	121.6(2)	122.7(4)		
N(3)–C(2)–Se(6)				120.7(3)
N(3)–C(4)–O(7)			125.5(3)	124.8(3)
N(3)–C(4)–S(7)	126.8(2)	127.8(4)		
C(5)–C(4)–O(7)			127.5(3)	128.9(3)
C(5)–C(4)–S(7)	126.6(2)	124.4(4)		
N(1)–C(5)–C(8)	110.3(2)	110.6(5)	111.1(3)	111.7(3)
N(1)–C(5)–C(9)	111.4(2)	110.6(5)	111.3(3)	111.3(3)
C(4)–C(5)–C(8)	112.9(3)	110.8(5)	110.6(3)	112.8(3)
C(4)–C(5)–C(9)	110.6(2)	112.3(5)	111.6(3)	109.2(3)
C(8)–C(5)–C(9)	111.2(3)	112.0(5)	111.8(3)	111.0(3)
I(2)–I(1)···S(6)	176.89(2)	177.94(4)	176.14(2)	
I(4)–I(3)···S(7)		173.74(4)		
I(2)–I(1)···Se(6)				173.84(1)
O(7)···H(3)–N(3)			153.6(4)$^{\mathrm{I}}$	

Symmetry codes: I $1 - x, 2 - y, -z$; II $2 - x, -y, -z$; III $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $1 + x, y, z$; V $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; VI $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; VII $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; VIII $x, 1 + y, z$; IX $-x, -y, -z$; X $-x, y - \frac{1}{2}, \frac{3}{2} - z$; XI $-x, -1 - y, 1 - z$; XII $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; XIII $1 - x, 1 - y, 1 - z$; XIV $-x, 1 - y, 1 - z$; XV $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; XVI $x, y - 1, z$; XVII $-x, \frac{3}{2} + y, \frac{3}{2} - z$; XVIII $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; XIX $1 - x, 1 - y, 2 - z$; XX $-x, -y - 2, 1 - z$.

other, while the mean plane defined by N(1), C(2), Se(6) and I(1) forms a dihedral angle of 7.9° with the ring plane, in accord with the displacement of selenium out of the ring plane. As found for the other structures, the Se···I–I fragment is once more not far from linearity [173.84(1) Å] (see Table 6).

^{13}C *Chemical Shifts*.—In order to determine the ^{13}C NMR chemical shifts of the 1:1 complexes for the thione compounds, the spectra of several solutions of the two reagents, obtained by adding increasing amounts of diiodine to a constant concentration of the organic molecule, were recorded in CH_2Cl_2 solution. The linear correlations of the ^{13}C NMR chemical shifts (δ) of C(2), C(4) and C(5) *versus* the concentration of the complex are collected in Fig. 3 for **1** and **2**. It has been preferred to optimize only the chemical shift of the adduct, by using the formation constants (K = 175 dm^3 mol^{-1} for **1** and 253 dm^3 mol^{-1} for **2**; 20 °C, CH_2Cl_2) obtained from the UV/VIS data,[1e] since in the NMR experiment, for solubility reasons, it was impossible to obtain experimental data in a very large range of the saturation fraction. The ^{13}C chemical shift of the free

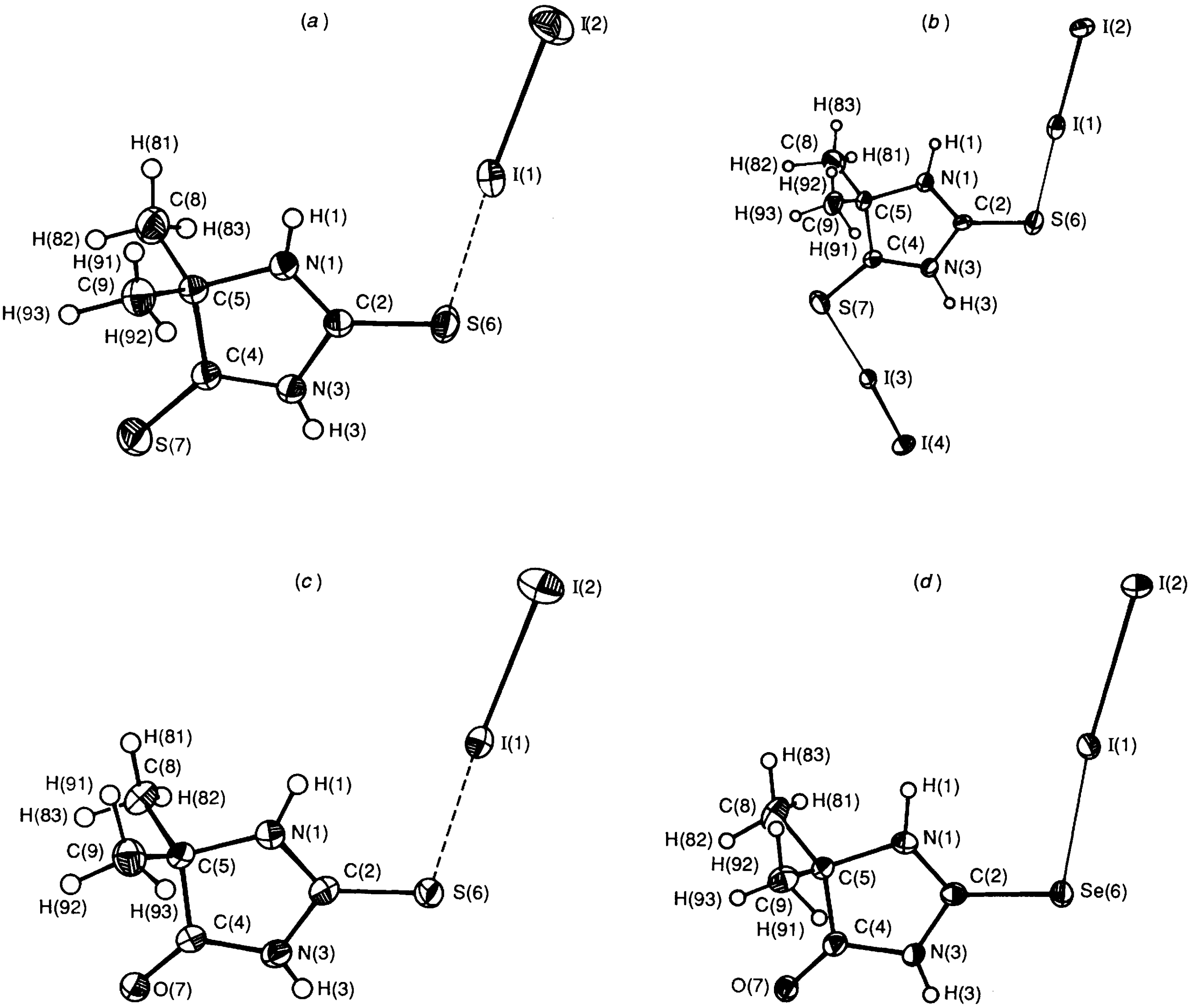

Fig. 1 An ORTEP[13] view of the molecular structures of (*a*) $\mathbf{1}\cdot I_2$, (*b*) $\mathbf{1}\cdot 2I_2$, (*c*) $\mathbf{2}\cdot I_2$ and (*d*) $\mathbf{3}\cdot I_2$. Thermal ellipsoids are drawn at the 30% probability level

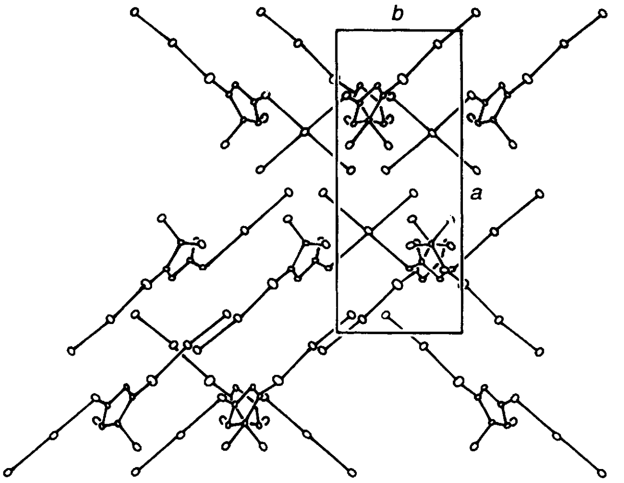

Fig. 2 Crystal packing of the compound $\mathbf{1}\cdot 2I_2$, showing the network of diiodine seen normally to the (110) plane

Table 7 The ^{13}C NMR chemical shifts (ppm) of the 1 : 1 c.t. complexes for the three donors

		1	**2**	**3**[a]
C(2)	*D*[b]	179.27	180.30	179.57
	$\Delta\delta^{\circ}$[c]	−1.795	−2.096	—
	r[d]	0.997	0.998	—
C(4)	*D*	210.31	177.23	176.96
	$\Delta\delta^{\circ}$	−1.399	−1.634	—
	r	0.993	0.998	—
C(5)	*D*	74.35	63.49	64.49
	$\Delta\delta^{\circ}$	1.428	1.137	—
	r	0.992	0.999	—
C(8), C(9)	*D*	27.78	23.85	23.25
	$\Delta\delta^{\circ}$	*e*	−0.128	—
	r	—	0.997	—

[a] The low solubility of the adduct of compound **3** prevented recording of its ^{13}C NMR spectrum. [b] *D* represents the ^{13}C chemical shift of the free donor. [c] $\Delta\delta^{\circ}$ is the variation of the chemical shift of the 1 : 1 c.t. complex from that of the free donor, as given by the slope in the linear correlation of δ *versus* the concentration of the complex. [d] *r* is the correlation coefficient of the straight line δ *vs.* [complex]. [e] No detectable variations were found.

donors, the $\Delta\delta^{\circ}$ (*i.e.* the variation of the chemical shift of the 1 : 1 complex with respect to the free donor) and the correlation coefficients of the straight lines δ/[complex] for Fig. 3 are reported in Table 7. Owing to the low solubility of the adduct of **3** it was impossible to record its ^{13}C NMR spectrum.

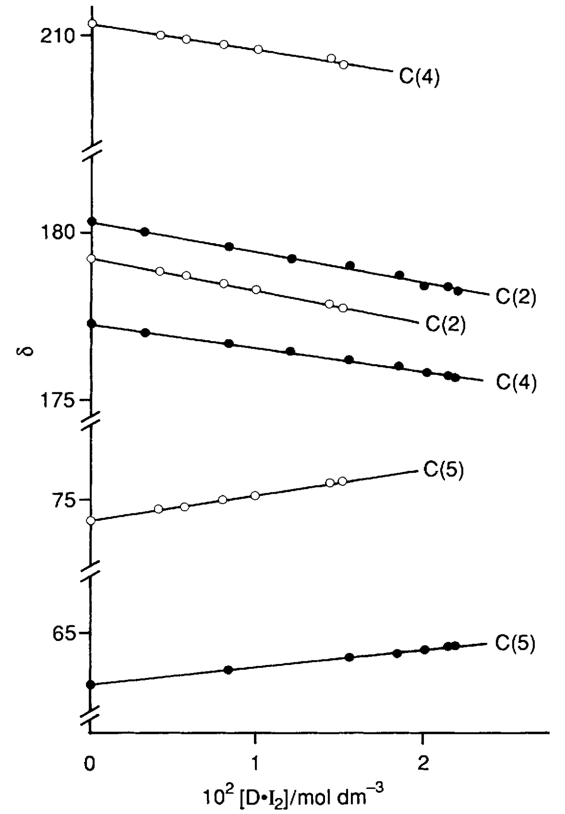

Fig. 3 The ^{13}C NMR chemical shifts of C(2), C(4) and C(5) for compounds **1** (○) and **2** (●) respectively as a function of the c.t. complex concentration [D•I$_2$]. All points have the same concentration of the thione compound and increasing amounts of diiodine. [**1**] = 1.87 × 10^{-2}; [**2**] = 2.33 × 10^{-2} mol dm^{-3}; CH_2Cl_2 solution; 20 °C. The spectrophotometric formation constants used in the calculation of [D•I$_2$] have been taken from ref. 1*e*

Table 8 Fourier-transform Raman bands (cm^{-1}) of the four crystalline compounds in the 350–50 cm^{-1} range

Compound	ν(I–I)	Other vibrations
1•I$_2$	152s	99w, 127w, 230w, 294vw, 336vw
1•2I$_2$	165s, 143ms	104w, 257w, 289vw, 331vw
2•I$_2$	158s	93vw, 134w, 232vw, 296vw, 308vw, 343vw
3•I$_2$	144s	82w, 108m, 256vw, 288w, 313vw

Table 9 Selected bond distances (Å) and angles (°), enthalpies of formation (ΔH_f) and dipole moments (μ), obtained from PM3 calculations on **1**•I$_2$, **2**•I$_2$ and a double NH···O hydrogen-bonded dimer of **2**•I$_2$

	1•I$_2$	**2**•I$_2$	Dimer of **2**•I$_2$
I(1)–I(2)	2.694	2.695	2.694
N(1)–C(2)	1.372	1.382	1.382
C(2)–N(3)	1.416	1.505	1.408
N(3)–C(4)	1.418	1.446	1.441
C(4)–C(5)	1.534	1.534	1.534
C(5)–N(1)	1.509	1.508	1.509
C(2)–S(6)	1.663	1.669	1.667
C(4)–O(7)		1.206	1.209
C(4)–S(7)	1.580		
S(6)···I(1)	2.661	2.653	2.657
N(1)–C(2)–N(3)	105.6	106.7	106.8
C(2)–N(3)–C(4)	114.1	111.9	111.7
N(3)–C(4)–C(5)	105.2	106.8	107.1
C(4)–C(5)–N(1)	102.0	100.7	100.6
C(5)–N(1)–C(2)	113.1	113.6	113.6
N(1)–C(2)–S(6)	131.1	128.8	128.8
N(3)–C(2)–S(6)	123.3	124.5	124.4
N(3)–C(4)–O(7)		121.5	121.6
C(5)–C(4)–O(7)		131.7	131.2
N(3)–C(4)–S(7)	125.7		
C(5)–C(4)–S(7)	129.1		
ΔH_f/kcal mol^{-1}	54.9	−17.6	−36.8
μ/D*	9.2	9.9	0.6

* D ≈ 3.33 × 10^{-30} C m.

Fourier-transform Raman Spectra.—The adduct bond formation between a donor and diiodine stabilizes the lone pair of electrons of the donor by mixing the donor orbital with the σ* antibonding orbital of I$_2$. One of the consequences of this is the lowering of the I–I bond order.[14] The more effective the interaction with the donor, the lower is the I–I bond order. Consequently, Raman spectroscopy provides a powerful tool to elucidate the interaction by means of the shifts of the ν(I–I) vibration in a complex with respect to that of free diiodine.[15–17] The Fourier-transform Raman spectral data for the four compounds are collected in Table 8 together with the assignments of the ν(I–I) vibrations. The spectra of **1**•I$_2$ and **2**•I$_2$ show strong bands at 152 and 158 cm^{-1} respectively, with overtones at 294 and 296 cm^{-1}, attributable to the ν(I–I) vibration. Two peaks at 143 ms and 165s cm^{-1}, with overtones at 289vw and 331vw cm^{-1}, are present in the Raman spectrum of **1**•2I$_2$, attributable to the two diiodine molecules bonded to S(6) and S(7), according to the different I–I bond lengths of 2.849(1) and 2.767(1) Å respectively. The Raman spectrum of compound **3**•I$_2$ shows a strong band at 144 cm^{-1} (with an overtone at 288 cm^{-1}), tentatively attributed to the ν(I–I) vibration. The medium band at 108 cm^{-1} could be indicative of the presence of the I$_3^-$ anion as a consequence of some decomposition, however no trace of I$_3^-$ was found in the X-ray crystal structure.

Semiempirical Calculations.—The PM3 semiempirical quantum-mechanical calculations[12] were carried out only on 5,5-dimethylimidazolidine-2,4-dithione–diiodine and 5,5-dimethyl-2-thioxoimidazolidin-4-one–diiodine in order to clarify the discrepancy between the S···I bond distances in the solid state and the corresponding interactions in CH_2Cl_2 solution measured as spectrophotometric stability constants.

Some selected bond distances and angles of the optimized geometries together with the calculated enthalpies of formation and dipole moments are collected in Table 9. In the same Table we also show the results of the calculations carried out on a model of the dimer of **2**•I$_2$ with two N–H···O hydrogen bonds as found in the solid state.

Discussion

The geometrical parameters for the interaction of thione and selone groups with the diiodine molecule are collected in Table 10. As regards the sulfur–diiodine interaction, the S···I–I arrangement is essentially linear and the values of *d*(S···I) and *d*(I–I) fall fairly close [18,*] to the hyperbola reported in ref. 3. The values of *d*(S···I) for the three reported structures are larger than those found in other charge-transfer complexes of thione compounds, *i.e.* 1,3-dimethylimidazole-2-thione–diiodine[3] (2.616 and 2.607 Å for the crystal modifications α and β respectively), ethylenethiourea[4] (2.487, 2.580, 2.588 Å), dithizone (phenylazothioformic acid 2-phenylhydrazide)[4]

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* The greater donor power of the thioketonic sulfur, the shorter is the S···I and the longer the I–I bond distance. However, this observation should not be overemphasized, since the the crystal packing can affect one or both of the distances.

Table 10 Geometrical parameters for the interaction of thione and selone groups with the diiodine molecule C=X ··· I(1)–I(2) (X = S or Se)

Compound	d[X ··· I(1)]/Å	d[I(1)–I(2)]/Å	X ··· I(1)–I(2)/°	C=X–I(1)/°	N–C=X ··· I* torsion angle/°
$1{\cdot}I_2$	2.748(1)	2.817(1)	176.89(2)	103.6(1)	6.3
$1{\cdot}2I_2$	2.737(1)	2.849(1)	177.94(4)	100.3(2)	11.0
	2.844(1)	2.767(1)	173.74(4)	105.6(2)	22.0
$2{\cdot}I_2$	2.773(1)	2.802(1)	176.14(2)	104.5(1)	0.4
$3{\cdot}I_2$	2.699(1)	2.962(1)	173.84(1)	100.1(1)	9.6

* The nitrogen used in the calculation of the torsion angle is that bonded to the hydrogen interacting with I(1) (see Fig. 1).

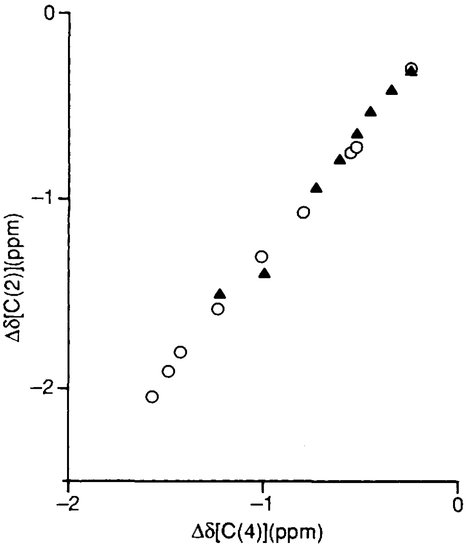
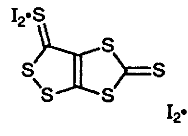


Fig. 4 The Δδ values (chemical shifts measured on solutions at different donor : diiodine ratios minus chemical shifts of the free donor) of C(2) as a function of the Δδ of C(4) for compounds **1** (○) and **2** (▲) respectively. The slopes 1.288 for **1** and 1.283 for **2** indicate that molecular diiodine affects the two donors in the same way and that C(2) is more affected than C(4). The correlation coefficients of the straight lines are 0.987 and 0.999 for **1** and **2** respectively



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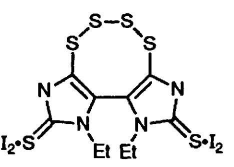

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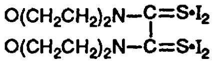

$$\begin{array}{l} O(CH_2CH_2)_2N{-}C{=}S{\cdot}I_2 \\ \qquad\qquad\quad | \\ O(CH_2CH_2)_2N{-}C{=}S{\cdot}I_2 \end{array}$$

5

(2.506–2.664 Å) and N-methyl-ε-thiocaprolactam[19] (2.688 Å); in all these cases the shorter bond distances agree well with the higher values of the formation constants[1a,19–21] of their complexes. The C(2)=S ··· I sulfur–iodine bond lengths of the three structures are fairly close to those reported for **3** [2.719(6) Å],[22] $(PhCH_2)_2S{\cdot}I_2$ (2.78 Å),[23] **4** [2.775(4) Å][24] and one of the bonds reported for **5** [2.789(6) Å],[25] while in $\mathbf{1}{\cdot}2I_2$ that of C(4)=S ··· I is of the same order of those reported for $2I_2$ c.t. complexes of compounds with thioether sulfur: 1,4-dithiane[26] [2.867(6) Å], dithia[3.3.1]propellane[27] [2.852(2), 2.806(2) Å] and dithia[3.3.2]propellane[27] [2.803(2), 2.902(4) Å].

However, the sulfur–diiodine bond distances of 2.748(1) and 2.773(1) Å in $\mathbf{1}{\cdot}I_2$ and $\mathbf{2}{\cdot}I_2$ respectively are not in accord with the values of the stability constants of the c.t. complexes obtained by spectrophotometric measurements in CH_2Cl_2 solutions.[1e] The K values are 199 ± 21 and 291 ± 22 dm^3 mol^{-1} at 17 °C for $\mathbf{1}{\cdot}I_2$ and $\mathbf{2}{\cdot}I_2$ respectively. As shown in Table 9, the PM3 semi-empirical calculation indicates a stronger interaction with diiodine in compound $\mathbf{2}{\cdot}I_2$ than in $\mathbf{1}{\cdot}I_2$, in agreement with the results obtained in solution and with the ionization energies measured by ultraviolet photoelectron spectroscopy.[18,]† In order to clarify the reasons for this anomaly, we have carried out a PM3 calculation on the dimer of $\mathbf{2}{\cdot}I_2$, with the two monomers linked by two NH ··· O hydrogen bonds, as realized in the solid state; as one can see in Table 10, the S ··· I bond distance undergoes a small but significant lengthening, which indicates that the hydrogen-bonding interaction is one of the factors which contribute to produce this discrepancy, although the interaction of diiodine with several atoms of the surrounding organic framework should not be underestimated.

The sulfur–diiodide interaction does not affect the C=S distances, which are not significantly changed with respect to the free donors [1.648(2) and 1.641(2) Å for C(2)–S(6) and C(4)–S(7) respectively in the free **1**,[28] 1.648(2) and 1.650(4) Å for C(2)–S(6) in 2-thiohydantoin[28] and in 3,5,5-trimethyl-2-thioxo-imidazolidin-4-one[29] respectively]. Except for $\mathbf{1}{\cdot}2I_2$ the torsion angles are close to 0° as also found for the ethylenethiourea compounds.[3]

The ^{13}C NMR resonances observed for the carbonyl and thiocarbonyl groups are slightly shifted upfield for the reported complexes (see Table 7), whereas the resonances of C(5) undergo very small downfield shifts and those of the methyl groups C(8) and C(9) remain practically unchanged. Similar but more consistent shifts were found in the ^{13}C NMR spectra of the complexes of imidazole-2-thione, 1-methylimidazole-2-thione and 1,3-dimethylimidazole-2-thione[3] in $(CD_3)_2SO$ solution. However, in assigning the resonances of the complexes Freeman *et al.*[3] did not take into account the dissociation equilibrium; the chemical shifts reported for the 2:1 and 1:1 (donor–diiodine) adducts must be interpreted only in terms of a displacement of the equilibrium towards complex formation.

The Δδ values (chemical shifts measured on solutions at different donor : diiodine ratios minus chemical shifts of the free donor) of C(2) as a function of the Δδ of C(4) are shown in Fig. 4 for the thione compounds. The slopes 1.288 for **1** and 1.283 for **2** indicate that I_2 affects C(2) more than C(4), in accordance with the interaction of diiodine with the heteroatom bonded to C(2). These data confirm the results on the interaction between **1** and diiodine in CH_2Cl_2 solution, obtained by UV/VIS spectroscopy.[1e] For **1**, the 1:1 model fitted very well the experimental absorbances and a 1:2 (donor–diiodine) complex was not detected in solution.[1e] On the other hand, the crystal data for $\mathbf{1}{\cdot}2I_2$ clearly show that the S(6) ··· I(1) interaction [2.737(1) Å] is stronger than the S(7) ··· I(3) one [2.844(1) Å].

The very short Se ··· I(1) bond distance in $\mathbf{3}{\cdot}I_2$ [2.699(1) Å] is consistent with the high stability constant of this complex[1e] and with the lengthening of the diiodine bond. Only a few structural data for complexes between compounds containing the selenoether group and molecular diiodine have been reported[30–33] and no data are available on the selenoxo group. As expected, the Se ··· I distances is shorter than those reported for selenoether compounds. In contrast with findings on thione compounds, in the selenium complex the strong Se ··· I

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† The stability constants, obtained in CH_2Cl_2, have been substantiated by the good correlation found between ln K and the ionization energies of the sulfur- and selenium-containing donors.

interaction affects the C=Se bond, which undergoes a lengthening from 1.805(8) Å in the free donor[28] to 1.861(4) Å in its adduct with diiodine.

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