Tetrahedron Vol. 35, pp. 511–514

0040–4020/79/0215–0511/$02.00/0

CHARGE TRANSFER COMPLEXES BETWEEN I_2 AND 1,3-IMIDAZOLIDINE-2-THIONE AND ITS N-MONO- AND N,N'-DI-SUBSTITUTED DERIVATIVES

FRANCESCO A. DEVILLANOVA and GAETANO VERANI
Istituto Chimico Policattedra, Via Ospedale 72, 09100 Cagliari, Italy

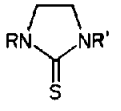
(*Received in UK* 12 *June* 1978)

Abstract—Spectrophotometric studies of iodine with 1,3-imidazolidine-2-thione and its N-mono- and N,N'-di-alkyl derivatives (alkyl = Me, Et) have been carried out in carbon tetrachloride and dichloromethane solutions. In each case, a new intense peak due to the charge transfer band of a 1:1 molecular complex was observed. The thermodynamic and spectral characteristics of these complexes have been determined. The well known "blue shift" of the visible band of I_2 is verified, but the analogous blue shift of the donor absorption is hidden by the solvents. To explain the very high differences between the stability constants of the N,N'-disubstituted derivatives and the others, an intramolecular H-bonding between NH and terminal iodine has been hypothesized. IR measurements carried out on N-ethyl-1,3-imidazolidine-2-thione seem to support this hypothesis.

For some time we have been interested in the coordination chemistry of some pentaatomic rings of general formula RN·CH_2·CH_2·X·CY (where for R = H, X = CH_2, O, S, NH, NMe, NEt; for R = Me, X = NMe, S; for R = Et, X = NEt; Y = S, Se) and we have found that they bind the metal ions by Y, although they have more coordinating sites.[1–3] On the other hand, molecules containing the thioamido group have a pronounced antithyroid activity and some of them, such as thiourea, thiouracil, imidazole-2-thione derivatives, etc. are used in clinical medicine.[4,5] It seems that their antithyroid activity is due to a competitive action with respect to a peroxidase by inhibiting the oxidation of the iodide; however the mechanism of the process is still not well known, but in any case the activity would be related to the facility to oxidize the thioamido group to disulphide.[5] For this purpose, it was considered of some interest to investigate the reaction between I_2 and the thioamido group in non polar solvents. In fact, it is well known that iodine forms 1:1 molecular complexes with molecules having lone pair electrons able to act as donors. In particular, it had been shown that amides and thioamides bind the I_2 by oxygen and sulphur respectively.[6–8] In this paper we will report the spectroscopic and thermodynamic properties of the adducts obtained by reacting I_2 with 1,3-imidazolidine-2-thione and its N-mono- and N,N'-disubstituted derivatives in CCl_4 and CH_2Cl_2 solutions. The aims of the work are to get information about the strength of the S–I link and to point out the influence of the substituents on the stability of the adducts.

RESULTS AND DISCUSSION

When 1:1 molecular complexes are formed between I_2 and donor molecules, the electronic spectrum will exhibit three distinct absorption bands;[6] two of them, the "blue shift" of the visible peak of I_2 and the charge transfer band, are normally observed, while the third, typical of the donor, is often hidden by the solvent. Here we shall report the results obtained by reacting I_2 with the following 1,3 - imidazolidines - 2 - thione:



R	R'	
H	H	1
Me	H	2
Et	H	3
Me	Me	4
Et	Et	5

in CCl_4 and CH_2Cl_2 solutions.[a] The imidazolidines show a very intense peak, not observable in CCl_4 solutions, falling below 250 nm which is probably a $\pi \rightarrow \pi^*$ transition of the =N–CS–N= chromophore,[9] although a blue shift is observed when using a more polar solvent (Table 1). In Fig. 1 the spectra of **5**, I_2 and their adduct are reported as examples. As described above, the C.T. band of the adduct and the blue shift band of I_2 are clearly visible as maximum and shoulder respectively, while the expected blue shift of the donor is masked by the solvent.

Figure 1 has been obtained by recording at 10° the spectrum of a solution containing an excess of ligand, using the proper amount of ligand in the range 240–390 nm and of I_2 in the range 390–450 nm as references, both of which are evaluated from the equilibrium constant.

Table 1. UV absorptions (nm) of 1,3 - imidazolidine - 2 - thione derivatives in different solvents (log ϵ in parentheses)

	MeOH	CH_2Cl_2	CCl_4
1	239(4.23)	248(4.29)	—
2	240(4.20)	247(4.27)	—
3	240(4.23)	248(4.27)	—
4	239(4.33)	245(4.35)	—
5	240(4.33)	247(4.36)	—

[a] All the compounds have been studied in CH_2Cl_2 since I is not soluble in CCl_4.

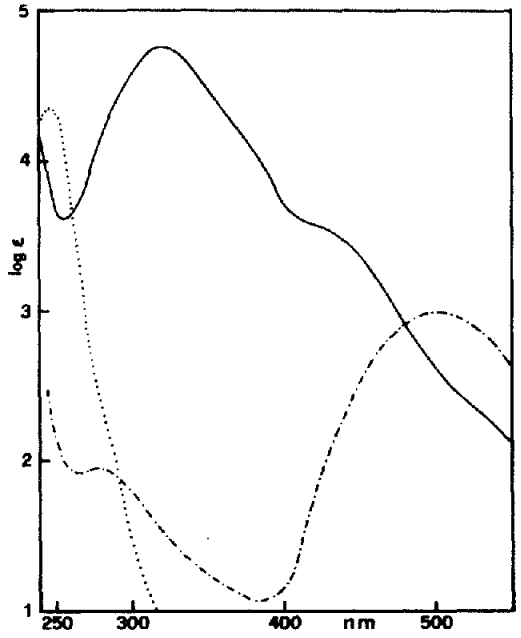


Fig. 1. UV visible spectra of **5** (. . . . .), I_2 (–.–.–.) and their adduct (———) in CH_2Cl_2 solutions.

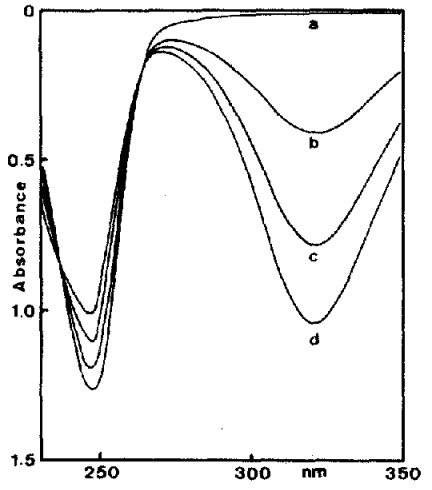


Fig. 2. Isosbestic points between the free **5** peak and the C.T. band in CH_2Cl_2 at 10.6°C. ([V] = $6.293 \cdot 10^{-5}$; (a) $[I_2] = 0.0$; (b) $[I_2] = 1.632 \cdot 10^{-5}$; (c) $[I_2] = 3.265 \cdot 10^{-5}$; (d) $[I_2] = 4.890 \cdot 10^{-5}$).

The wavelengths of the maxima of the C.T. bands and the I_2 blue shifts together with the respective log are reported on Table 2 for all the compounds.

In methylene chloride solutions, three isosbestic points are present; the first two occur between the donor absorption and the C.T. band; the other is due to the bands of the free and bonded I_2. Only this last isosbestic is visible in CCl_4 solutions. The isosbestic points are shown for **5** in Figs. 2 and 3.

The presence of the isosbestic points indicates that in all cases one molecule of I_2 is added to the ligand. Hence, the equilibrium reaction is:

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

where D is one of the donors. From the equilibrium, the following equation can be written:[6]

$$\frac{I \cdot D}{A} = \left(I + D - \frac{A}{\epsilon}\right)\frac{1}{\epsilon} + \frac{1}{K \cdot \epsilon} \qquad (2)$$

where I and D are the initial molar concentrations of iodine and the donor respectively, A is the absorbance due to the complex, ϵ is the molar extinction coefficient of the complex and K is the equilibrium constant. When $D \gg I$, the equation becomes:

$$\frac{I \cdot D}{A} = \frac{D}{\epsilon} + \frac{1}{K \cdot \epsilon} \cdot \qquad (3)$$

The eqns (2) and (3) are straight lines when $I \cdot D/A$ is reported against $(I + D - (A/\epsilon))$ or D; from these, ϵ and K can be evaluated. Here, an iterative process using the equation (2) was employed until constant values for ϵ and K (the complete description is given in the experimental section) were reached.

The ln K, obtained at different temperatures in the range 10–45°, against 1/T gave straight lines, from which $\Delta H°$ and $\Delta S°$ were evaluated. For the sake of brevity, in Table 3 only the K's at 25° are reported together with the thermodynamic parameters. As shown by the K values, the solvents stabilize the adducts in a different manner, the complexes being more stable in CH_2Cl_2 than in CCl_4 solutions.

The most important feature, which arises from Table 3, is the considerable difference in stability constants between the adducts of N,N′-disubstituted derivatives and all the others. *A priori* one should expect the sulphur donor ability in **1–5** to change within a small range, when

Table 2. Spectral properties of 1:1 molecular complexes

	1		**2**		**3**		**4**		**5**	
	CCl_4[a]	CH_2Cl_2	CCl_4	CH_2Cl_2	CCl_4	CH_2Cl_2	CCl_4	CH_2Cl_2	CCl_4	CH_2Cl_2
C.T. band(nm)	—	298	304	298	304	299	325	322	327	321
$\sim \log \epsilon$[b]	—	4.65	4.65	4.66	4.51	4.64	4.57	4.58	4.55	4.70
Isosbestic points(nm)	—	239	—	238	—	234	—	237	—	236
	—	256	—	257	—	260	—	261	275	262
	—	454	473	454	474	452	480	476	488	474
I_2 blue shift(nm)	—	396	415	394sh	415	396sh	438	417sh	440	420sh
$\sim \log \epsilon$[c]	—	3.50	3.50	3.53	3.44	3.52	3.40	3.55	3.37	3.58

[a] Not soluble.

[b] Obtained by averaging among all the values obtained at different temperatures.

[c] Obtained by recording the spectrum at 10.6°C of a known amount of adduct, using in the reference cell an amount of I_2, calculated from the equilibrium constant at the same temperature.

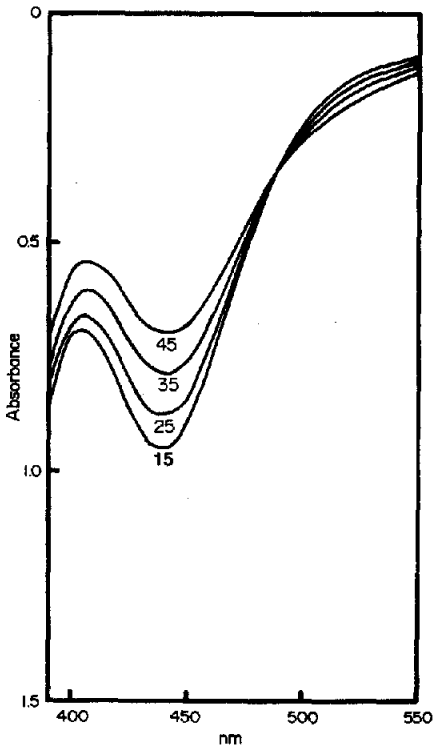
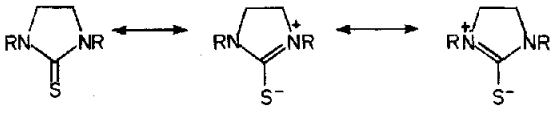


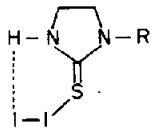
Fig. 3. Isosbestic point between the I_2 visible peak and the blue shift of I_2 obtained by reacting I_2 with **5** ($[I_2] = 3.24 \cdot 10^{-4}$; $[5] = 2.325 \cdot 10^{-3}$) at 15, 25, 35 and 45° in CCl_4 solution.

one considers that the inductive effect of the alkyl works in the opposite way with respect to the steric effect. On the other hand, if one supposes that the inductive effects are predominant, **4** and **5** will have the highest values in contrast with what we have found; *vice versa*, if the steric ones are predominant, **3** can not have the highest value.

In order to explain the different donor ability of sulphur between thiourea and thioacetamide towards I_2, Lang[6] invoked the three components to the resonance for thiourea in comparison with the two for thioacetamide; consequently, sulphur in the former is the best donor. Also in **1–5** there are three components to the resonance where the zwitterionic forms give a very high contribution,[10,11] evaluated for **1** in the solid state of *ca.* 80%.[12] In this view, **1–5** should be expected to behave as thiourea. But, the association constant of thiourea (8500 $l \cdot mole^{-1}$ at 20°) is fairly close to those of **4–5**.



The very high stability of **1–3** adducts can be explained by hypothesizing an intramolecular H–bonding between the NH hydrogen and the terminal iodine:



This seems to be confirmed by IR spectroscopy, carrying out the spectra on the N–Et derivative[b] in CCl_4 solution in presence of and without the stoichiometric amount of I_2. Figure 4 shows that **3** has two very strong absorptions over 3000 cm^{-1} due to νNH, whose relative intensities depend on the concentration. The neat band at 3465 cm^{-1} is due to the free NH, whereas the broad absorption at 3220 cm^{-1} is typical of νNH with H–bonding. When I_2 is added to **3**, the neat band at 3465 cm^{-1} is split (Fig. 4e). One of the two bands remains unshifted, while the other falls at 3395 cm^{-1}, indicating H– bonding. This bond must be intramolecular, since the solutions are dilute enough to show the ligand to be completely free[c] (lack of the band at 3220 cm^{-1} in (d)).

The $\Delta H°$ and $\Delta S°$ values, reported in Table 3, are in agreement with the above hypothesis. In fact, in **1–3**, the $\Delta S°$'s are lower than those of **4–5**, confirming a higher final order in the former than in the latter derivatives. At the same time the $\Delta H°$'s agree with bonds which are more stable in **1–3** than in **4–5**.

[b] Among **1–3** N-ethyl 1,3-imidazolidine-2-thione is the most soluble in CCl_4.

[c] It was impossible to record solutions with adduct concentrations higher than $\sim 1 \times 10^{-3}$ moles/l because of turbidity.

Table 3. Association constants ($l \cdot mole^{-1}$) at 25°C and thermodynamic parameters for 1:1 molecular complexes[a]

Compound	Solvent	K	$-\Delta H°$[c]	$-\Delta S°$[d]
1[b]	CCl_4	—	—	—
2	"	14550 ± 450	10.8 ± 0.3	17.1 ± 1.0
3	"	33100 ± 1400	11.0 ± 0.4	16.1 ± 1.3
4	"	3050 ± 120	8.1 ± 0.3	11.1 ± 1.0
5	"	3100 ± 140	7.9 ± 0.5	10.9 ± 1.2
1	CH_2Cl_2	50600 ± 1300	11.0 ± 0.3	15.4 ± 1.1
2	"	49500 ± 1500	14.2 ± 0.6	26.5 ± 1.9
3	"	82750 ± 1700	14.9 ± 0.7	27.6 ± 2.4
4	"	8100 ± 350	9.0 ± 0.8	12.3 ± 2.7
5	"	8520 ± 200	8.9 ± 0.3	11.9 ± 1.1

[a] $\Delta H°$ and $\Delta S°$ are evaluated from the plot ln K vs 1/T, using the data obtained at four temperatures in the range 10–45°. All the correlation coefficients fall in the range 0.997–1.000.

[b] Not soluble.

[c] Kcal/mole.

[d] cal/K · mole.

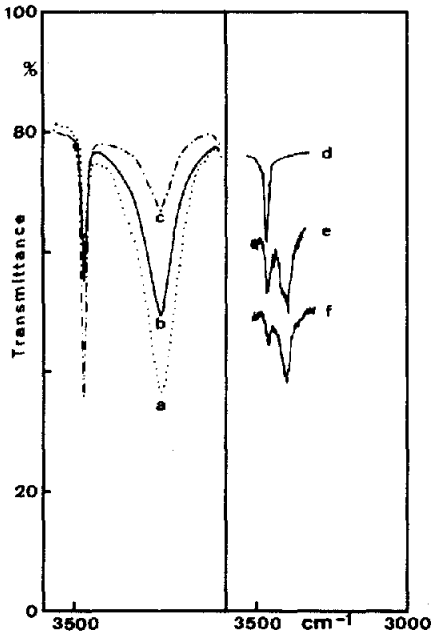


Fig. 4. IR spectra of **3** in CCl_4 solutions: (a) 0.123 moles/l in a 0.05 mm KBr cell; (b) $6.15 \cdot 10^{-2}$ moles/l in a 0.1 mm KBr cell; (c) $6.15 \cdot 10^{-3}$ moles/l in a 1.0 mm KBr cell; (d) $1.23 \cdot 10^{-3}$ moles/l in 1.0 mm KBr cell; (e) adduct obtained from **3** and I_2 at the same concentrations of (d) (the signal was twice amplified); (f) as (e) with an excess of I_2.

However, the thiourea, which in the same manner might give rise to intramolecular H– bondings with the terminal iodine, unexpectedly gives rise to stability constants very far from **1–3**, and its enthalpy ($\Delta H^\circ = -9.6$ in CH_2Cl_2) is close to **4–5**. This fact might be due to a great variety of possible H– bondings both among the NH_2 groups and between these and the terminal iodine. Vice versa, the rigidity of the pentaatomic rings favours the closing of a 6-membered ring by a H---I intramolecular bond, excluding any other considerable interaction of NH.

EXPERIMENTAL

Materials. Twice sublimed iodine was purified by sublimation from KI and stored in a desiccator. N-Mono- and N,N'-disubstituted derivatives of 1,3-imidazolidine-2-thione were prepared and purified according to literature.[13–15] All the solns were prepared by weighing the materials and diluting in volumetric flasks. The iodine solns were checked by titration with arsenious acid.

Data treatment. For each compound four solns with the same concentration of I_2 and different excesses of the ligand were used. These solns were recorded around the C.T. bands at four different temps in the range 10–45°. The absorbance values used for the calculation of K and ϵ were read at the maximum of C.T. band and 5 nm before and after the maximum. In order to evaluate K and ϵ the eqn (2) was employed, using an iterative process until consistent values of K and ϵ were obtained. The iterative process required two ÷ four subsequent cycles, 10^{10} has been used as an ϵ starting value in the first cycle. When consistent values were reached, the output of the program gave ϵ, K, the correlation coefficient of the eqn (2) and the concentration of the adduct for each solution.

In all cases, correlation coefficients ranging between 1.000 ÷ 0.998 were obtained.

The K's, used in the Van't Hoff's plot, were obtained by averaging the values at different wavelengths. The accuracy of these results was confirmed by the fact that the concentrations of the adduct evaluated at different wavelengths were practically the same.

The ϵ values at the maximum wavelength of the C.T. band, reported in Table 2, were obtained by averaging among all the values obtained at different temps.

All the isosbestic points between the C.T. band and the absorption of the ligands were obtained by recording the spectra of several solns, prepared with the same quantity of ligands and different amounts of I_2 (in defect with respect to the ligand).

The isosbestic point between the visible peak of I_2 and its blue shift band was obtained by recording the spectra of a soln at various temps.

Instruments. UV visible spectra were recorded on a Perkin–Elmer 402 instrument, connected to a Lauda K2RD thermostat.

IR spectra were recorded on a Perkin–Elmer 325.

The experimental data were processed by a 370/135 I.B.M. calculator.

REFERENCES

[1]F. A. Devillanova and G. Verani, *J. Coord. Chem.* **7**, 177 (1978).
[2]F. A. Devillanova and G. Verani, *Transition Met. Chem.* **3**, 42 (1978); and refs. therein.
[3]F. A. Devillanova and G. Verani, *Inorg. Chim. Acta* **30**, 209 (1978).
[4]K. Hofmann, *The Chemistry of Heterocyclic Compounds*, Part I, p. 89. A. Weissberger, Interscience, London (1953).
[5]L. S. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics*, 5th Edn. Macmillan, New York (1975).
[6]R. P. Lang, *J. Am. Chem. Soc.* **84**, 1185 (1962).
[7]K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy and C. N. R. Rao, *Trans. Faraday Soc.* **62**, 788 (1966) and refs. therein.
[8]R. A. Zingaro and W. C. Cooper, *Selenium*. Van Nostrand-Reinhold, New York (1974).
[9]C. N. R. Rao, *Ultra-Violet and Visible Spectroscopy*, 2nd Edn. Butterworths, London (1967).
[10]F. A. Devillanova and G. Verani, *J. Chem. Soc.* Perkin II, 1529 (1977).
[11]F. A. Devillanova and G. Verani, *J. Chem. Res.* (*S*) **24**, (*M*) 0239–0250 (1978).
[12]P. J. Wheatley, *Acta Cryst.* **6**, 369 (1957).
[13]A. F. McKay and M. E. Kreling, *J. Org. Chem.* **22**, 1581 (1957).
[14]L. Maier, *Helv. Chim. Acta* **53**, 1417 (1970).
[15]G. D. Thorn, *Can. J. Chem.* **33**, 1278 (1955).