Charge Transfer Complexes Between Iodine and the Thioamido Entity Contained in some Pentaatomic Rings

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Spectrophotometric investigations on the adducts of iodine with pyrrolidine-2-thione, 1,3-oxazolidine-2-thione, 1,3-thiazolidine-2-thione and N-methyl-1,3-thiazolidine-2-thione have been carried out in carbon tetrachloride and dichloromethane solutions. These complexes show a very intense peak, due to the charge transfer band, and the well known "blue shift" of the visible band of iodine, whereas the analogous shift of the ligand is masked from the solvents. Their thermodynamic and spectral characteristics have been determined and compared with those of the series of 1,3-imidazolidine-2-thione.

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For some time (1-6) we have been interested in the chemistry of the following pentaatomic rings containing the thioamido group:

X	R		X	R	
CH$_2$	H	I	NH	H	V
O	H	II	NMe	H	VI
S	H	III	NEt	H	VII
S	Me	IV	NMe	Me	VIII
			NEt	Et	IX
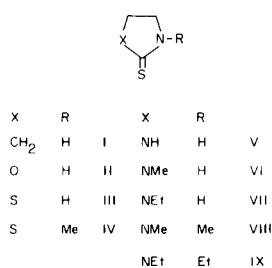
From ir investigations (1-3), it has been pointed out that the X substituent in ring affects the π-bond order on the CS link. In particular, this seems to be close to a single bond in the imidazolidines (V-IX) (2), whereas it retains some double bond contributions in I-IV (1,3-4). Of course, the electron density at the sulphur atom must depend on the X substituent. In order to check the charge on the sulphur atom, we thought of considering the donor ability of the thioketonic sulphur with iodine for the above molecules. In fact, it is well known that the donor ability of sulphur decreases in the order $RS^- > R_2S > R_2C=S > > S$ in ring (7), with the consequence that a decrease of the bond order on $C=S$ requires an increase of the charge on sulphur and a stronger bond with the acceptor.

Here, we wish to report the results obtained by the reaction of I-IV with iodine in carbon tetrachloride and dichloromethane solutions and compare them with those of V-IX, previously reported (8). This study was stimulated by the biological interest (9-11) of molecules having the thioamido entity. In particular, some of them have pronounced antithyroid activity. For this purpose, this property seems to be related to the facility of the oxydation of the thioamido group to disulphide (11) and consequently to the negative charge on the thioketonic sulphur.

Compounds I-IV show two absorption bands, whose wavelengths decrease with the increase in the polarity of

the solvent (see Table 1). The first peak, very intense (log ϵ $\sim$ 4.2), is attributed to a $\pi \rightarrow \pi^*$ transition and the other (log ϵ $\sim$ 2) to an n$\rightarrow \pi^*$ transition according to the literature (12-13). The uv spectra of the ligands are completely modified when iodine is added, in consequence to the formation of adducts. As previously described (8,13-15), the iodine is bonded through the thio-ketonic sulphur atom to form 1:1 molecular adducts, as confirmed by the presence of isosbestic points. In the analogous derivatives of V-IX (8) three isosbestic points were found, the first two between the band of the free ligand and the charge transfer band of the adduct, and the other between the free iodine and its "blue shifted" band. Also, II has similar isosbestic points in dichloromethane solution, whereas I, III and IV show only the isosbestic point relative to free and bonded iodine (see Table 2). In carbon tetrachloride solution only this last isosbestic is visible for all the compounds, indicating that in any case 1:1 molecular complexes are formed, according to the reaction:

$$D + I_2 \rightleftharpoons D \cdot I_2$$
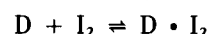
where D is one of the donors. As an example, the spectrum of the reaction between IV and iodine in carbon tetrachloride, recorded at various temperatures, is reported in the Figure.

The equilibrium constants have been evaluated by using the equation (14):

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

where I and D are the initial molar concentrations of iodine and the donor respectively, A is the absorbance of the complex, ϵ is the molar extinction coefficient of the complex and K the equilibrium constant. When we studied V-IX, the calculations were carried out using the absorbances of the maximum of the C.T. band, since iodine and the ligands here show low absorptions. On the contrary, I-IV have valuable molar extinction coefficients at the wavelengths corresponding to the charge transfer

Table 1

Uv Absorptions (nm) in Different Solvents (log ϵ)

	Methanol		Dichloromethane		Carbon Tetrachloride	
I	2.66 (4.15)	316 (1.85)	270 (4.18)	338 (1.68)	273 (4.19)	334 (1.96)
II	243 (4.28)	277 sh (2.40)	247 (4.32)	283 sh (2.30)	(a)	
III	274 (4.19)	323 (2.09)	279 (4.18)	339 (2.05)	283 (4.14)	347 (2.18)
IV	271 (4.17)	323 (2.07)	273 (4.19)	334 (2.08)	281 (4.16)	345 (2.14)

(a) Not soluble.

Table 2

Spectral Properties of 1:1 Molecular Complexes

| | I | | II | | III | | IV | |
	Carbon Tetrachloride (a)	Dichloromethane	Carbon Tetrachloride (a)	Dichloromethane	Carbon Tetrachloride	Dichloromethane	Carbon Tetrachloride	Dichloromethane
C.T. Band (nm)	—	297	—	299	306	302	310	308
~ Log ϵ (b)	—	4.72	—	4.57	4.54	4.43	4.49	4.70
Isosbestic Point (nm)	—	426	—	476 (d)	476	456	462	460
Iodine Blue Shift (nm)	—	394	—	410	420	406	426	412
~ Log ϵ (c)	—	3.68	—	3.42	3.48	3.61	3.58	3.57

(a) Not soluble enough. (b) From the adduct spectra recorded using the proper amount of ligand calculated from the K in the reference cell. (c) From the calculations. (d) In dichloromethane solution, II shows two other isosbestic points at 242 and 258 nm.
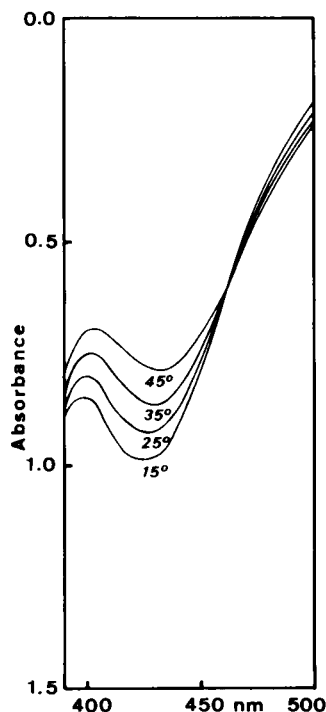
Isosbestic Point between the Iodine Visible Peak and the Blue Shift of Iodine Obtained for IV ([IV] = 3.339 × 10⁻² and [I₂] = 3.24 × 10⁻⁴) in Carbon Tetrachloride at 15, 25, 35, and 45°.

bands. For this reason we have chosen the iodine blue shifted band to carry out the calculations. From the straight lines, obtained by plotting I • D/A versus (I + D -A/ϵ), ϵ and K can be evaluated (see Experimental). The ϵ values, thus obtained and averaged on the different temperatures, are reported in Table 2. The association constants at different temperatures are reported in Table 3, together with the thermodynamic parameters obtained by the Van't Hoff's plot. As found for the imidazolidine series (8), the adducts increase their stability with the solvent polarity.

It should be expected that the association constants vary with the donor ability of the sulphur (7) in agreement with its charge density. Obviously, this increases with the electron releasing power of the X substituent in ring. In this view, the highest association constants are found for I, the lowest for 1,3-oxazolidine-2-thione in agreement with the strong electronegativity of the oxygen. However, there is a very high difference in the stability constants between I and the others, which have similar K values. In particular, I shows K's of the same order as those found for N-monosubstituted and unsubstituted 1,3-imidazolidines-2-thione (V-VII) (8). There, the very high stability constants for V-VII was interpreted by hypothesizing an interaction by intramolecular hydrogen bonding between the terminal iodine and the NH hydrogen to form a six

Table 3

Association Constants (ℓ•moles^{-1}) for 1:1 Molecular Complexes at Various Temperatures and $\Delta H°$ and $\Delta S°$ Parameters

Temperature (°C)	I		II		III (a)		IV	
	Carbon Tetrachloride	Dichloromethane	Carbon Tetrachloride (b)	Dichloromethane	Carbon Tetrachloride	Dichloromethane	Carbon Tetrachloride	Dichloromethane
15.7	—	74900 ± 2200	—	1120 ± 40	3490 ± 200	—	352 ± 16	2000 ± 38
20.1	—	—	—	—	2456 ± 180	4180 ± 200	—	1575 ± 35
25.0	—	40050 ± 1800	—	705 ± 15	—	—	181 ± 15	—
30.0	—	—	—	—	1415 ± 80	1994 ± 150	—	815 ± 20
34.5	—	21700 ± 1500	—	460 ± 10	—	—	116 ± 10	—
39.4	—	—	—	—	801 ± 40	1087 ± 45	—	545 ± 17
44.3	—	12460 ± 800	—	302 ± 10	—	—	71 ± 3	403 ± 25
ϱ	—	1.000	—	1.000	.999	1.000	.997	.998
$\Delta H°$ (c)	—	-11.5 ± .4	—	- 8.3 ± .2	-10.9 ± .6	-12.6 ± .9	-10.0 ± 0.6	-10.2 ± .2
$\Delta S°$ (d)	—	-17.4 ± 1.5	—	-14.9 ± .8	-21.6 ± 1.9	-26.6 ± 2.9	-23.2 ± 1.8	-20.1 ± .8

(a) The adduct of III with iodine has been previously studied by Bhaskar, et al. (13), in chloroform solution. The $K_{25°}$ (1460 ℓ•mole^{-1}) and the $\Delta H°$ (-10.0 Kcal mole^{-1}) agree well with our data. (b) Not soluble. (c) Kcal/mole. (d) Cal/°K•mole.

membered ring. The ir spectra, carried out only on VII (soluble enough in carbon tetrachloride) seemed to support this hypothesis (8).
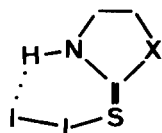
The same hypothesis could be formulated in order to explain the difference in constant stability values between III and IV. In fact, the inductive effect of the methyl group in IV would enhance the negative charge on the exo-sulphur atom and a higher association constant should be expected for IV. Conversely, $K_{III} > K_{IV}$ and this could be justified only accounting for an intramolecular interaction, as suggested for V-VII. A confirmation of this by means of ir spectroscopy has not been possible owing to the very low solubility of III in both the solvents.

In this view, II also would be expected to be stabilized by intramolecular hydrogen interaction. However, II has the lowest association constants among I-IX. This is explainable by considering that the inductive effect of the oxygen in ring determines the lowest density charge on the thio-ketonic sulphur.

A direct measurement of the interaction between the donors and iodine is given by $\Delta H°$'s. From Table 4, one can see that IV, VIII and IX (donors without NH) have low $\Delta H°$ absolute values. Since the negative charge on the sulphur atom is larger in VIII and IX rather than in IV (1-2), one would expect the reverse sequence. However, the lower absolute values for the disubstituted imidazolidines can be ascribed to the steric hindrance of the two alkyl groups. The $\Delta S°$ values seem to support this view.

Among the donors with NH, which interacts with the terminal iodine, the sequence of the enthalpies agree sufficiently with the electronic effects of the X substituent in ring. On the whole, we observe that the $-\Delta S°$ values are higher here than for the donors without NH, thus indicating much more ordered adducts.

EXPERIMENTAL

Materials.

The iodine solutions were prepared and tested as previously described (8). Compounds I-IV were synthesized according to the literature (16-19). All the solutions were prepared by weighing the materials and diluting them in volumetric flasks.

Data Treatment.

For each compound several solutions with the same concentration of iodine and different excesses of the ligand were used. The spectra were recorded at different temperatures in the range 10-45°. The absorbance values used for the calculation of K and of the molar extinction coefficient of the adduct were read at different wavelengths around the maximum of the iodine blue shifted band. In order to evaluate K and ϵ, equation (2) was employed, using an iterative process until their consistent values were reached. In all cases, correlation coefficients within 1.000 ÷ 0.997 were found.

The two isosbestic points between the charge transfer band and the absorption of the free II were obtained by recording the spectra of several solutions, prepared with the same quantity of ligand and different amounts of iodine (in defect with respect to the ligand). For I, III and V, which present the $\pi \rightarrow \pi^*$ band close to the charge transfer band, the analogous isosbestic points were not well identified.

The isosbestic point between the visible peak of iodine and its blue shifted band was obtained by recording the spectra of a same solution at various temperatures (see Figure). These were also obtained by recording the spectra of several solutions, having different amounts of ligand and the same quantity of iodine (in defect with respect to the ligand).

Instruments.

Uv-visible spectra were recorded on a Perkin-Elmer 402 instrument, connected to a Lauda K2RD thermostat. The data were processed by a 370/135 I.B.M. calculator.

Table 4

Thermodynamic Parameters for 1:1 Molecular Complexes of I-IV
and 1,3-Imidazolidine-2-thione and its N-mono and N,N'-Disubstituted Derivatives

| | R | X | -$\Delta H°$ | | -$\Delta S°$ | |
			Carbon Tetrachloride	Dichloromethane	Carbon Tetrachloride	Dichloromethane
I	H	CH_2	—	11.5 ± .4	—	17.4 ± 1.5
II	H	O	—	8.3 ± .2	—	14.9 ± .8
III	H	S	10.9 ± .6	12.6 ± .9	21.6 ± 1.9	26.6 ± 2.9
IV	CH_3	S	10.0 ± .6	10.2 ± .2	23.2 ± 1.8	20.1 ± .8
V	H	NH	—	11.0 ± .3	—	15.4 ± 1.1
VI	H	NMe	10.8 ± .3	14.2 ± .6	17.1 ± 1.0	26.5 ± 1.9
VII	H	NEt	11.0 ± .4	14.9 ± .7	16.1 ± 1.3	27.6 ± 2.4
VIII	Me	NMe	8.1 ± .3	9.0 ± .8	11.1 ± 1.0	12.3 ± 2.7
IX	Et	NEt	7.9 ± .5	8.9 ± .3	10.9 ± 1.2	11.9 ± 1.1

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