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CHARGE TRANSFER COMPLEXES BETWEEN I_2 AND SELENOAMIDO ENTITY CONTAINED IN SOME PENTAATOMIC RINGS

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Abstract—Spectrophotometric studies on the charge transfer complexes between molecular iodine and some pentaatomic rings containing the selenoamido entity, i.e. $\overline{X \cdot CH_2 \cdot CH_2 \cdot NR \cdot C} = Se$ (where for R = H, X = CH_2, NH, NMe, NEt, S; for R = Me, X = NMe, S; for R = Et, X = NEt) have been carried out in CCl_4 and CH_2Cl_2 solutions. The presence of isosbestic points are indicative of 1:1 molecular adducts.

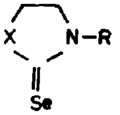
The simultaneous determination of the stability constants (K) and molar extinction coefficients (ϵ) has been carried out by using no linear least square methods. In order to improve the reliability of K and ϵ a criterion for selecting the experimental points is reported. The association constants obtained for the present compounds and the thioketonic isologues are correlated with the ionization energies of the lone pairs of the exoatom.

Recently[1,2] we have studied the adducts obtained by reaction of molecular iodine with the following pentaatomic rings $\overline{RN \cdot CH_2 \cdot CH_2 \cdot X \cdot C} = Y$ (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). In all cases, 1:1 molecular adducts were formed, with the iodine bonded to the thioketonic sulphur. The association constants for the reaction

$$\overline{RN \cdot CH_2 \cdot CH_2 \cdot X \cdot C} = S + I_2 \rightleftarrows \overline{RN \cdot CH_2 \cdot CH_2 \cdot X \cdot C} = S \cdot I_2 \qquad (1)$$

were obtained by spectrophotometric measurements; these values made it possible to measure quantitatively the influence of the X substituent on the sulphur donor ability towards the iodine. Really, the association constants K of (1) strongly change with X, i.e. for R = H the values of K increase in the order $O < S < CH_2 < NH \sim NMe < NEt$ and range from 705 for $>$O to 82750 l moles^{-1} for $>$NEt, at 25° in CH_2Cl_2 solutions. Then the reaction with I_2 can be considered as a powerful method of measuring the donor ability of the thioketonic sulphur. By considering the donors without NH, a decrease of K was observed in contrast with the well known electronic-realising effect of the alkyl groups. This was interpreted as being due to the presence of an intramolecular H-bonding between NH and the terminal iodine, only possible with donors having the NH group. This investigation has been stimulated in view of the increasing importance of molecules containing the thioamido entity in biological systems. Particularly, similar molecules are already used in clinical medicine for their pronounced antithyroid activity.[3] Since this activity seems to be related to the facility of the thioamido group of oxidizing to disulphide, it seemed interesting to extend this kind of study to the analogous selonic compounds, being selenium more oxidable than sulphur.

We here wish to report the results obtained by reacting molecular iodine with the following compounds:



X	R	
CH_2	H	1
NH	H	2
NMe	H	3
NEt	H	4
NMe	Me	5
NEt	Et	6
S	H	7
S	Me	8

with the purpose of evidentiating the difference in donor properties between sulphur and selenium.

RESULTS AND DISCUSSION

All the ligands show absorption bands, whose wavelengths decrease with the increase in the polarity of the solvent (Table 1). The imidazolidines have a unique peak attributable to a $\pi \rightarrow \pi^*$ transition of the $=N \cdot CSe \cdot N=$ chromophore in analogy with the sulphur isologues.[1] These peaks fall at higher wavelengths than those of the imidazolidine-2-thione derivatives, in agreement with the higher polarizability of the Se atom.

The same is found for **1**, **7** and **8**, which show two or three absorptions. The band at lower energy is attributable to the $n \rightarrow \pi^*$ transition, while the others are probably due to $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions.[4]

Some spectral properties of the charge transfer complexes obtained by reaction of **1–8** with molecular iodine in carbon tetrachloride and dichloromethane solutions are reported in Table 2. The presence in all cases of one or several isosbestic points are indicative of the formation of only 1:1 molecular adducts, i.e. also here the reaction is of the type (1).

For **1**, **7** and **8** only one isosbestic point, i.e. that

Table 1. U.V. absorptions (nm) in different solvents (log ε in parentheses)

Compound	MeOH	CH_2Cl_2	CCl_4
1	294(4.08)348sh(2.40)	301(4.13)382(2.34)	309(4.01)346sh(3.31)
2	257(4.07)	271(4.16)	-
3	257(4.09)	267(4.12)	280(4.28)
4	259(4.07)	269(4.19)	281(4.32)
5	256(4.19)	265(4.21)	281(4.32)
6	258(4.11)	267(4.22)	281(4.32)
7	253(3.75)305(4.12)356(2.55)	251sh313(4.15)378(2.51)	320(4.20)396(2.50)
8	262(3.94)301(4.14)352sh(2.39)	257(3.88)306(4.10)374(2.45)	3.14(4.16)396(2.52)

Table 2. Spectral properties of 1:1 molecular complexes (log ε in parentheses)

Compound	C.T. band(nm)		Isosbestic points (nm)		I_2 blue shifted band (nm)	
	CCl_4	CH_2Cl_2	CCl_4	CH_2Cl_2	CCl_4	CH_2Cl_2
1	-	-	-	476	-	-
2	-	306(4.66)[a]	-	260-277-474	-	368(4.23)
3	315(4.49)[a]	307(4.70)[a]	287-488	260-276-474	352sh(4.20)	372sh(4.05)
4	316(4.71)[a]	307(4.71)[a]	288-488	257-276-476	352sh(4.27)	370sh(4.05)
5	303(4.50)	322(4.55)	490	275-482	370(4.33)[a]	356sh(4.23)
6	303(4.50)	324(4.47)	490	260-275-482	374(4.34)[a]	354sh(4.28)
7	-	b	-	480[c]	-	352sh(4.28)
8	322(4.32)[d]	328(4.81)[e]	-	490	364sh(4.2)[c]	354sh(4.69)[e]

a) The ε values are averaged from those obtained at 17° and 35°C.

b) The maximum of the C.T. band and the ε value are difficult to determine in this adduct.

c) This isosbestic has been found by recording freshly prepared solutions having an excess of I_2 with respect to the ligand, since they decompose.

d) These values are only indicative, since the adduct slowly decomposes.

e) The ε values may contain relevant errors, since they are evaluated on the basis of the value of the molar extinction coefficients at 345 nm reported in Table 3.

between the visible peak of I_2 and its blue shifted band, is present. In addition to this, the imidazolidines exhibit two other isosbestic points, relative to the absorptions of the free and bonded ligands. Two typical patterns for 2 are reported in Figs. 1 and 2. For 1, 7 and 8 the first two isosbestic points are not present since the CT band overlaps that of the free ligand and the molar extinction coefficients of the adduct are higher with respect to those of the free ligand and so we always observe an increase of absorbance at each wavelength of the examined range.

The very high values of the stability constants of the adducts allow a careful determination of the molar extinction coefficients and a poor reliability of the K's (Experimental). The graphical and linear least square methods, previously used for the thioketonic derivatives,[1,2] did not give encouraging results in this case. Recently, Carta and Crisponi[5] have developed a new approach to the problem of the simultaneous determination of K and ε for equilibria of the type (1) based on the definition of the β parameter as $\beta = K^{-1}[(a+b+1/K)^2 - 4ab]^{-(1/2)}$ (where a and b are the

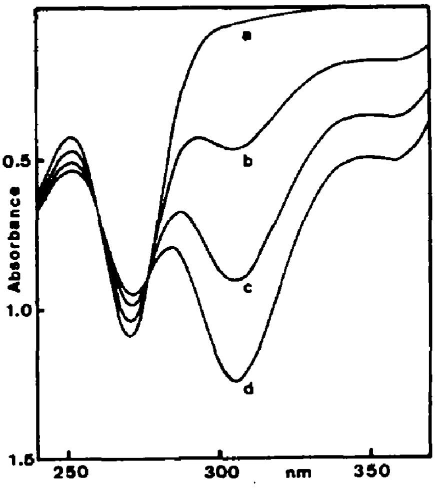


Fig. 1. Isosbestic points between the free 2 band (271 nm) and the C. T. band of its adduct with iodine (306 nm); [2] = 7.592 10^{-5} M; [I_2] in increasing amount from (a) to (d); CH_2Cl_2; 20.

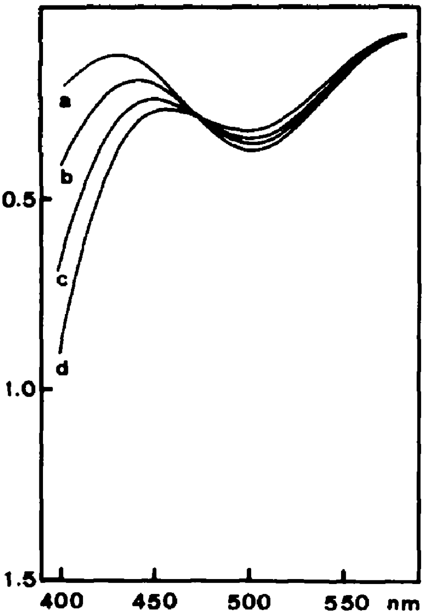


Fig. 2. Isosbestic point between the free and bonded iodine for 2; $[I_2] = 4.32\ 10^{-4}$; [2] in increasing amount from (a) to (d); CH_2Cl_2; 20°.

initial concentrations of the reagents). β is regarded as the independent variable of the system. In fact, they have demonstred that, by using the Gauss-Newton linearization method[6], the analytical expressions of the error matrix, neglecting the experimental errors, can be written in terms of β as

$$S_K^2 = \frac{S^2K^2}{\sum(\beta-\bar{\beta})^2} \qquad S_\epsilon^2 = S^2\cdot\epsilon^2\cdot\frac{\overline{\beta^2}}{\sum(\beta-\bar{\beta})^2} \tag{2}$$

where S_K and S_ϵ are the errors on K and ϵ respectively, $S^2 = \Sigma(Ac-As)^2/(N-2)$ Ac and As being the calculated and experimental absorbances, $\bar{\beta} = \Sigma\beta/N$, $\overline{\beta^2} = \Sigma\beta^2/N$ and N the number of experimental points. These equations are identical to those obtained for a linear regression[7], where β is the independent variable. Equations (2) show that $\Sigma(\beta-\bar{\beta})^2$ must be as great as possible in order to lower the errors of K and ϵ. This means that it is opportune to choose the experimental points with β far from $\bar{\beta}$.

We have selected the experimental points in order to have the β range as large as possible. The working range of β is reported in the sixth column of Tables 3 and 4. In the last columns of the same tables the interval of the saturation fraction, defined with respect to the reagent at the lower concentration, is reported together with K and ϵ.

Table 3. Stability constants and ϵ values of the adducts between the selonic derivatives and I_2 in CH_2Cl_2 solutions

Compound	t (°C)	$K \cdot 10^{-5}$ ($\ell\cdot$moles^{-1})	λ (nm)	ϵ_λ ($\ell\cdot$moles^{-1}cm^{-1})	β^a	s^b
2	17.0	19.17±2.54	306	47740±290	.017- .189	.983- .747
	34.6	8.95±1.02		44360±360	.036- .262	.963- .654
3	17.0	34.62±4.14	307	51740±220	.007- .146	.993- .803
	35.0	18.44±1.30		48360±160	.013- .349	.986- .535
4	17.0	23.85±9.30	307	51040±500	.014- .311	1.000- .726
	35.0	7.13± .68		50400±260	.037- .310	.975- .586
5	17.0	4.95± .22	322	35500±140	.041- .367	.958- .482
	35.0	2.24± .23		35040±410	.083- .374	.914- .587
6	17.0	10.89±1.05	324	28340±150	.049- .240	.915- .619
	35.0	3.20± .20		30020±370	.044- .329	.957- .587
7	17.0	.42± .09	370	21220±1500	.270- .629	.696- .229
	35.0^c	-		-	-	-
8	17.0	.37± .06	345	43900±2880	.338- .783	.596- .139
	35.0^d	.14± .09		42900±16000	.517- .877	.396- .075

a) see text for its definition

b) saturation fraction defined as ratio between the complex concentration and that of the reagent at lower concentration.

c) the adduct of 7 is unstable and decomposes fastly at 35°C.

d) also the adduct of 8 with I_2 is unstable, and this explain the high errors both on K and ϵ

Table 4. Stability constants and ϵ values of the adducts between the selonic derivatives and I_2 in CCl_4 solutions(a)

Compound	t (°C)	$K \cdot 10^{-5}$ ($\ell \cdot moles^{-1}$)	λ (nm)	ϵ_λ ($\ell \cdot moles^{-1} \cdot cm^{-1}$)	β	a
3	17.0	5.19±.17	315	48860±160	.056- .359	.952- .569
	35.0	2.31±.89		48680±3150	.109- .469	.882- .369
4	17.0	5.10±.15	316	51620±160	.047- .347	.951- .572
	35.0	1.79±.08		51520±350	.114- .536	.878- .369
5	17.0	6.52±.30	370	22260±50	.008- .479	.992- .469
	35.0	2.22±.24		20420±700	.279- .420	.613- .437
6	17.0	6.15±.17	374	22780±50	.000- .539	1.000- .340
	35.0	2.01±.44		21040±95	.002- .393	1.000- .524

a) The adducts of 1, 7 and 8 decompose; 2 is not soluble in CCl_4.

The ϵ values obtained at the two temperatures are generally close, with a low degree of uncertainty; *vice versa* the K's are sometimes affected by high errors; to improve their reliability, a larger β range should be explored, but in the present case, experimental constraints prevented us from enlarging this range. However, it is interesting to note that the selonic compounds give more stable adducts than the corresponding sulphur isologues,[1,2] thus indicating that the Se–I bond is stronger than the S–I one. This is also deducible from the comparison of the wavelengths of the I_2 blue shifted bands in the two series of the considered compounds; in fact they fall within 394–420 nm in CH_2Cl_2 and 415–440 nm in CCl_4 for the thioketonic derivatives,[1,2] and within 352–374 nm in the selonic ones (Table 2). As far as regards the influence of the X substituent on the donor properties of the selenium atom, we note that the thiazolidines have lower stability constants than those of imidazolidines, thus confirming the previous results obtained for the analogous S compounds. This fact well agrees with the charge density on Se which is higher in imidazolidines than in thiazolidines.[8]

The studies on the corresponding thioketonic compounds[1,2] showed that for the same X substituent, the ligands with R=H have higher stability constants than those with R = alkyl. By IR spectroscopy this was proved to be due to an H-bonding between the NH and the terminal I atom. Also here, in CH_2Cl_2, we observe a decrease of the K values on passing from monosubstituted imidazolidines and thiazolidine to N,N'-di-substituted imidazolidines and N-methyl-thiazolidine. However this is not verified in CCl_4 solution.

From the K values the thermodynamic parameters have been obtained and are reported in Table 5. Obviously, a rough estimate of the K's produces high uncertainty on ΔH° and ΔS°, although the obtained values are usual for similar reactions.

To conclude, the reaction of the adduct formation between these molecules and I_2 makes it possible to measure quantitatively the donor properties of the exocyclic atom Y with respect to X. Therefore, correlations between the stability constants and other properties related to the charge density of Y are to be expected. Really, a linear relation between the lnK versus the

Table 5. Association constants at 25° for 1:1 molecular complexes of I_2 and selonic derivatives and thermodynamic parameters

Compound	Carbon Tetrachloride			Dichloromethane		
	K	−ΔH°	−ΔS°	K	−ΔH°	−ΔS°
1	-	-	-	-	-	-
2	-	-	-	$1.34 \cdot 10^6$	7.7	-2.3
3	$3.58 \cdot 10^5$	8.0	1.4	$2.59 \cdot 10^6$	6.2	-8.5
4	$3.15 \cdot 10^5$	10.3	9.5	$1.37 \cdot 10^6$	11.9	11.9
5	$3.97 \cdot 10^5$	10.6	10.0	$3.44 \cdot 10^5$	7.8	.9
6	$3.68 \cdot 10^5$	11.0	11.6	$6.20 \cdot 10^5$	12.1	14.0
7	-	-	-	-	-	-
8	-	-	-	$2.37 \cdot 10^4$	9.6	12.0

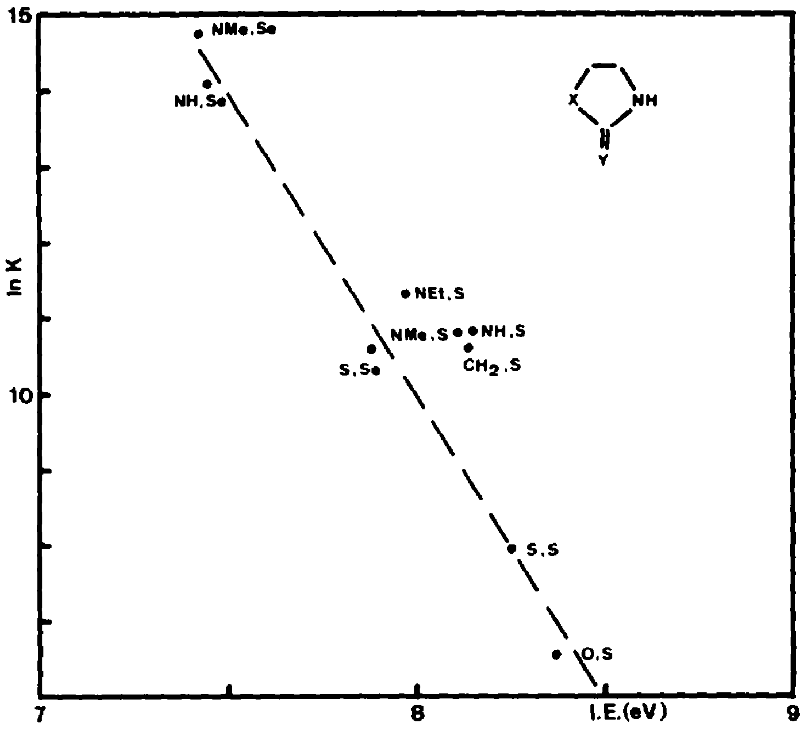


Fig. 3. Linear correlation between lnK and ionization energy of the lone pair (n) of Y. Each compound is labelled by the couple of the substituents (X, Y).

ionization energy[8] (I.E.) of the lone pair of the Y atom has been found (see Fig. 3); such a correlation confirms the realibility of the calculated K's.

EXPERIMENTAL

Materials. Twice sublimed I_2 was purified by sublimation from KI and stored in desiccator. All the Se compounds were prepared and purified according to lit.[12-16] All the solns were prepared by weighing the materials and diluting them in volumetric flasks immediately before their utilization, since they slowly decompose giving off red Se. However, this decomposition is very fast for **1**, **7** and **8** in CCl_4 for which it was not possible to calculate the association constants. Also **1** decomposes in CH_2Cl_2.

Data treatment. All the isosbestic points between the CT band and the absorption of the ligands were obtained by recording the spectra of several solns, prepared with the same quantity of ligand 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 shifted band was obtained by recording the spectra of several solns with the same quantity of I_2 and different amounts of donor in defect with respect to I_2.

For very high stability constants, the ϵ values are carefully detectable, but the K's are very uncertain as extensively discussed by several authors.[9-11]

We have determined the ϵ values for all the compounds by working in two different manners: (i) several solutions with the ligand in excess with respect to I_2 in different amounts were prepared and recorded at several temperatures in the 10-45° range; with the decrease of the temp, the absorbance values of each solution increase tending to a constant value. From this, for each soln the ϵ values have been calculated and averaged on all the solutions; (ii) several solns, containing the same amount of I_2 and increasing concentrations of the ligand, still in excess with respect to I_2, were recorded; the absorbance due to the complex increases with the increasing of the ligand concentration up to a constant value. The ϵ's calculated in this way correspond to those found in (i).

In order to improve the reliability of the stability constants (i.e. to enlarge the β range) it was necessary to work with cells having optical paths of 1, 5 and 10 cm. In all cases the absorbance values ranged within 0.4-1.0.

Association constants and molar extinction coefficients have been calculated by non-linear least squares, using a FORTRAN program that can utilize either a procedure proposed by Conrow *et al.*,[17] or the Gauss-Newton linearization method. Both methods converge to the same K and ϵ estimates; however the first was chosen for its shorter time of calculation. The final ϵ values obtained by this treatment of the absorbance data are consistent with those obtained experimentally. The reported errors on K and ϵ are the diagonal elements of the variance-covariance matrix calculated with the Gauss-Newton linearization method.

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

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