Molecular Adducts between Iodine and Some Benzazole-2-thione and -2-selone Derivatives

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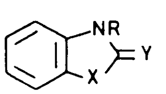
Spectrophotometric studies of adducts obtained by reacting molecular iodine and some benzazole-2-thione and -2-selone derivatives have been carried out in CH_2Cl_2 solutions. The thermodynamic and spectral characteristics of these complexes have been determined. Except for benzoxazole-2-selone and 3-methylbenzothiazole-2-selone, at least one isosbestic point has been found in the spectra of all the compounds, indicating the formation of a 1 : 1 molecular adduct. This model, employed for the calculation of the stability constants, fits the experimental data well in all cases. A non-linear least-squares method has been used for the calculation, and attention has been taken in selecting the experimental points to improve the reliability of the *K* and ε values.

For some years we have been interested in the chemistry of the thio- and seleno-amido groups contained in heterocyclic penta-atomic molecules with general formula $R\overline{N\cdot CH_2\cdot CH_2\cdot X\cdot C}{=}Y$ (where R = H, Me, and Et; X = CH_2, O, S, Se, NH, NMe, and NEt; Y = O, S, and Se). Among other studies, we have measured[1–3] the co-ordinating abilities of Y by evaluating the stability constants (*K*) of their 1:1 molecular adducts with I_2. The results show that the stability of these complexes depends on the charge density of the donor atom and then on the *endo*-substituent X. For this reason, empirical correlations can be found between the *K* values and molecular properties related to the Y charge density.[4] In a previous paper,[3] for example, a good linear correlation was found between ln *K* and the ionization energy of the lone pair of Y both for thione (Y=S) and selone (Y = Se) derivatives.

The presence of a benzene ring condensed with various azole systems seems to affect the donor properties of Y considerably. In order to determine this change quantitatively, we have studied the adduct formation between such donors and molecular iodine. For this study, compounds (**1**)—(**14**) were used.

The study consists of the simultaneous determination of the stability constant and of the molar extinction coefficient (ε) of the adducts by spectrophotometric data. However, the evaluation of *K* and ε may lead to erroneous results if the experimental points are chosen incorrectly. For this purpose, many authors[5–7] have considered the reliability of *K* and ε, giving criteria for the choice of reagent concentrations. Among these, the most important is to consider the widest possible range of saturation fractions, *i.e.* to take into account several solutions ranging from a very low adduct concentration to complete transformation of one of the reagents into the complex. With this in view, we have followed Carta and Crisponi's suggestion[5,6] as far as possible for the choice of the experimental points.



Y = S	R	X	Y = Se
(1)	H	NH	(**2**)†
(3)	H	NMe	(**4**)
(5)	Me	NMe	(**6**)
(7)	H	O	(**8**)
(9)	Me	O	(**10**)
(11)	H	S	(**12**)†
(13)	Me	S	(**14**)

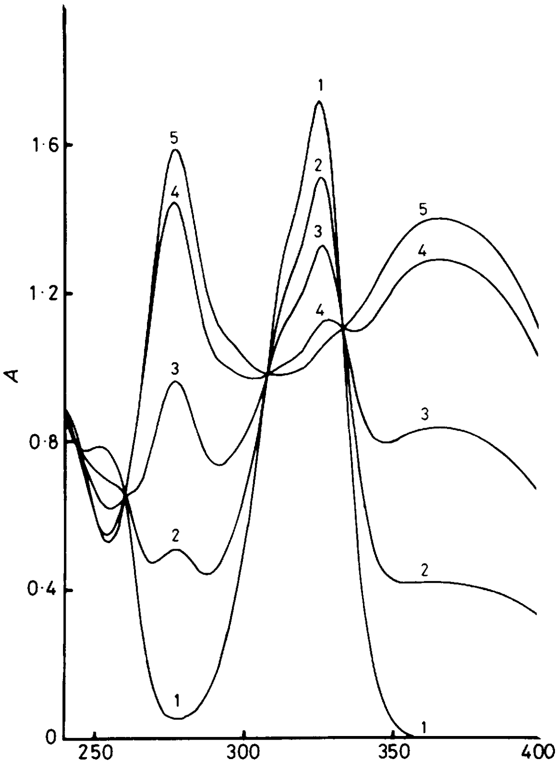


Figure 1. Isosbestic points between the absorption of the free (**6**) (curve 1) and its $D\cdot I_2$ complex in CH_2Cl_2. [(**6**)] 5.321×10^{-5} and [I_2] 1.625×10^{-5}, 3.25×10^{-5}, 4.875×10^{-5}, 6.5×10^{-5}M for curves 2—5, respectively

Results and Discussion

Experimental measurements were carried out in CH_2Cl_2 solutions. All compounds, except (**8**) and (**14**), show the presence of isosbestic points, which indicate the formation of the 1:1 molecular adduct: $D + I_2 \rightleftharpoons DI_2$ where D, I_2, and DI_2 are the donor, molecular iodine, and the adduct. As an example, the three isosbestic points found for (**6**) are reported in Figure 1 and for all the complexes in the last column of Table 1. The absorption bands of the ligands and their adducts are also collected in Table 1. As described in a previous paper,[3] for the simultaneous determination of the equilibrium constant (*K*) and the molar extinction coefficient of DI_2, we have followed the criteria outlined by Carta and Crisponi,[5] who demonstrated

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† This compound is not stable in CH_2Cl_2 solution.

Table 1. U.v.-visible absorptions of the free ligands and their 1:1 molecular adducts with I_2 in CH_2Cl_2 (log ε in parentheses)

Compound *	Ligand bands (nm)	Adduct bands (nm)	Isosbestic points (nm)
(**1**)	254(4.03), 303sh(4.44), 310(4.55)	284(4.39), 316(4.66)	485
(**3**)	250(4.19), 304sh(4.47), 312(4.59)	285(4.44), 314(4.71), 370(4.23)	491
(**5**)	247(4.29), 304sh(4.42), 313(4.55)	270(4.26), 282sh(4.21), 369(4.53)	295, 319, 505
(**7**)	258(4.31), 264(4.77), 296sh(4.41), 301(4.44), 306(4.42)	271(4.55), 318(4.84)	486
(**9**)	259(3.68), 264(3.63), 303(4.14)	270(4.28), 315(4.49)	498
(**11**)	281(3.29), 328(4.51)	284(4.49), 343(4.66), 400sh(3.97)	491
(**13**)	243(4.22), 327(4.51)	258(4.27), 284(4.41), 338(4.67), 396sh(4.08)	493
(**4**)	324(4.43)	296(4.43), 325(4.62), 390(4.18)	250
(**6**)	314sh(4.40), 325(4.51)	276(4.48), 362(4.43)	260, 308, 333
(**8**)	266(3.50), 319(4.55)	278(4.69), 335(4.64)	
(**10**)	267(3.56), 318(4.53)	280(4.32), 343(4.53), 390sh(4.14)	307, 322, 496
(**14**)	351(4.50), 388(3.36)	267(4.21), 295(4.58), 357(4.63), 410sh(4.17)	

* Compounds (**2**) and (**12**) are not stable in CH_2Cl_2 solutions; however, even though (**8**) decomposes, its decomposition rate at 17 °C is slow enough to allow these measurements.

Table 2. Stability constants (l mol^{-1}) at 17 and 35 °C for 1:1 molecular adducts. The ε values are referred to the wavelengths used for the data treatment. For the definition of the *G* and *s* parameters see Experimental section

Compound	λ/nm	*t*/°C	ε/l mol^{-1} cm^{-1}	*K*/l mol^{-1}	*G*	*s*
(**1**)	410	17	6 725 ± 320	$(6.61 \pm 1.49) \times 10^4$	0.13—0.74	0.87—0.15
		35	6 680 ± 380	$(2.96 \pm 0.53) \times 10^3$	0.25—0.85	0.75—0.08
(**3**)	390	17	12 045 ± 360	$(1.74 \pm 0.23) \times 10^4$	0.02—0.71	0.98—0.17
		35	11 775 ± 390	$(6.12 \pm 0.56) \times 10^3$	0.06—0.86	0.94—0.07
(**5**)	370	17	34 900 ± 655	$(7.12 \pm 0.27) \times 10^3$	0.03—0.73	0.97—0.17
		35	31 370 ± 670	$(2.93 \pm 0.11) \times 10^3$	0.03—0.85	0.97—0.09
(**7**)	410	17	3 720 ± 60	$(7.62 \pm 0.23) \times 10^1$	0.12—0.91	0.88—0.06
		35	3 385 ± 130	$(4.38 \pm 0.28) \times 10^1$	0.18—0.95	0.82—0.03
(**9**)	350	17	17 965 ± 1 100	$(7.52 \pm 1.03) \times 10^1$	0.33—0.95	0.67—0.04
		35	17 365 ± 1 900	$(4.11 \pm 0.74) \times 10^1$	0.47—0.96	0.53—0.02
(**11**)	410	17	8 015 ± 155	$(8.51 \pm 0.49) \times 10^2$	0.03—0.80	0.97—0.11
		35	8 035 ± 210	$(3.51 \pm 0.21) \times 10^2$	0.06—0.90	0.94—0.05
(**13**)	390	17	13 700 ± 400	$(9.21 \pm 1.30) \times 10^2$	0.16—0.82	0.84—0.11
		35	13 770 ± 620	$(3.98 \pm 0.55) \times 10^2$	0.16—0.91	0.84—0.05
(**4**)	390	17	13 890 ± 575	$(1.52 \pm 1.81) \times 10^6$	0.01—0.17	0.99—0.72
		35	13 730 ± 660	$(4.41 \pm 2.46) \times 10^5$	0.02—0.30	0.98—0.54
(**6**)	380	17	26 040 ± 410	$(1.46 \pm 0.41) \times 10^6$	0.00—0.25	1.00—0.61
		35	25 230 ± 440	$(3.67 \pm 0.59) \times 10^5$	0.01—0.45	0.99—0.38
(**8**)	390	17	13 630 ± 900	$(8.12 \pm 1.11) \times 10^3$	0.14—0.63	0.85—0.28
		35				
(**10**)	390	17	14 630 ± 970	$(4.54 \pm 0.73) \times 10^3$	0.15—0.83	0.85—0.10
		35	12 410 ± 1 170	$(2.14 \pm 0.38) \times 10^3$	0.27—0.91	0.73—0.05
(**14**)	295	17	42 200 ± 1 500	$(1.02 \pm 0.19) \times 10^5$	0.04—0.51	0.96—0.41
		35	36 800 ± 500	$(3.88 \pm 0.18) \times 10^4$	0.09—0.70	0.91—0.18

the utility of a *G* parameter to select the experimental points. In terms of *G*, the errors in *K* and ε decrease with the increase of $\Sigma(G - \bar{G})^2$ (where $\bar{G} = \Sigma G/N$ and N = number of data points). The working ranges of *G* are reported in Table 2, together with the saturation fraction *s* defined with respect to the reagent of lower concentration.

The calculations have been carried out at the wavelengths reported in Table 2, where the difference between the molar extinction coefficients of the complex and the reagents is a maximum. In Table 2, the ε and *K* values obtained at 17 and 35 °C are also reported. It is interesting that the calculated ε values at the two temperatures are very close except for (**5**) and (**14**), whose values differ by *ca.* 11% and 15%, respectively. The reliability of the *K* values can be shown graphically by reporting the sum of the squared deviations (χ^2) between the calculated and the experimental absorbances as a function of *K*. In Figure 2 such a deviation is given as R_{χ^2} [$= \chi^2(K)/\chi^2(K_0)$, *i.e.* as the ratio between the sums of the squared deviations calculated for K and K_0, where K_0 is the best value of *K*] for the thione compounds; the deeper the hole, the more reliable the calculated *K*. As one can see, (**5**) gives the best value, and (**1**) and (**9**) the worst. Generally, the selones show worse values of R_{χ^2}, since experimental constraints prevented us from achieving a wider *G* interval.

The stability constants strongly depend on Y and X substituents. *exo*-Substitution of the selenium with the sulphur atom increases the *K* values by *ca.* 10^2, whereas, in both series, *endo*-substitution increases *K* in the order O < S < NR. In Table 3, the stability constants at 25 °C obtained in the present work are compared with those previously reported [1-3] using the azolidine ring as substrate. A general trend for the thiones is that on passing from the azolidines to the benzazole derivatives the stability constants are decreased thus showing a decrease in the donor ability of the thione sulphur; this lowering is larger for the compounds containing an NH group. The different donor ability of the sulphur in the two series of compounds can be related to the strength of the $>$C=S bond. Structural data indicate that this bond is shorter in the benzazole than in the

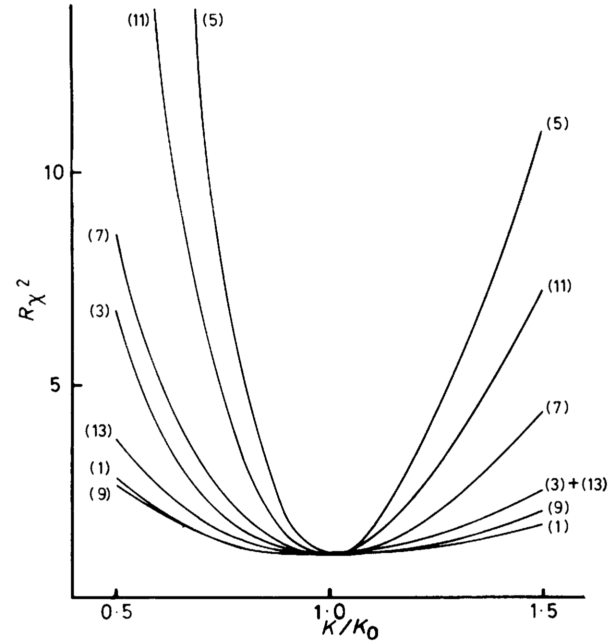
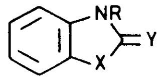
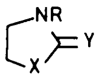


Figure 2. R_{χ^2} *versus* K (ranging from 0.5 K_o to 1.5 K_o) for the sulphur derivatives. R_{χ^2} is defined as $\chi^2(K)/\chi(K_0)$, where $\chi^2(K)$ and $\chi^2(K_0)$ represent the summation of the squared deviations of the experimental absorbances and those calculated by using K and K_0 as equilibrium constants, where K_0 is the best fit value

Table 3. Stability constants (l mol^{-1}; 25 °C) of the adducts with I_2 of the benzazole and azolidine derivatives

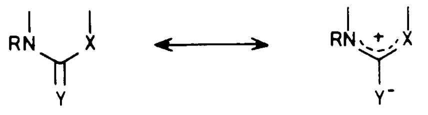




R	X	Y = S	Y = Se	Y = S	Y = Se
H	NH	4.57×10^3		5.06×10^4	1.34×10^6
H	NMe	1.08×10^4	8.61×10^5	4.95×10^4	2.59×10^6
Me	NMe	4.74×10^3	7.74×10^5	8.10×10^3	3.44×10^5
H	O	5.91×10^1		7.05×10^2	
Me	O	5.70×10^1	3.21×10^3		2.17×10^4*
H	S	5.67×10^2		2.89×10^3	
Me	S	6.26×10^2	6.54×10^4	1.15×10^3	2.37×10^4

* The adduct between I_2 and *N*-methyloxazolidine-2-selone has been studied in the present work. In this case, the presence of three isosbestic points at 262, 276, and 485 nm is indicative of a 1 : 1 molecular adduct. The evaluated stability constants at 17 and 35 °C are $(3.37 \pm 0.17) \times 10^4$ and $(1.29 \pm 0.5) \times 10^4$ l mol^{-1}, respectively.

azolidine derivatives: for example in (**1**)[8] it is 1.671 Å and in the corresponding ethylenethiourea[9] 1.708 Å. This means that the contribution to the resonance of the zwitterionic form (**15**) is more important in the azolidines than in the benzo-derivatives. This is also supported by the change in the carbon–nitrogen bond; in fact this varies in the opposite way, 1.362 Å for (**1**) and 1.322 Å for ethylenethiourea. An increase in the zwitterionic form produces an increase in the positive charge on the NH hydrogen (when R = H) and, consequently, favours a hydrogen bonding interaction with the terminal iodine of Y–I–I. The strengths of the Y–I and NH ··· I bonds seem to be synergic, since the higher the Y donor ability the higher the positive charge on the NH hydrogen and also the higher the intramolecular hydrogen bonding with the terminal iodine. These considerations agree with the large reduction in the K values for the compounds containing an NH group on passing from azolidines to benzazoles; in fact, in the latter compounds the decrease in the K values is due both to a lower donor ability of the thione sulphur and to a lowering of the hydrogen bond interactions.



(**15**)

However, on passing from the azolidine- to the benzazole-2-selone derivatives the trend is not so simple, since (**4**) and (**10**) undergo a decrease while (**6**) and (**14**) show an increase of the K values.

Experimental

Materials.—Iodine was purified by sublimation from KI and stored in a desiccator. Benzoxazole-2-thione (**7**), benzothiazole-2-thione (**11**), and its 3-methyl derivative (**13**) were supplied by Fluka and further recrystallized several times from water–ethanol. Benzimidazole-2-thione (**1**), and its 1-methyl (**3**) and 1,3-dimethyl (**5**) derivatives, were prepared and purified according to the literature.[10,11] 3-Methylbenzoxazole-2-thione (**9**) was synthesized by isomerization of 5-methylbenzoxazole-2-thione[12,13] in presence of MeI and purified by recrystallization from benzene. The 2-selone isologues (**2**), (**4**), (**8**), and (**12**) were obtained by the procedure outlined by Warner[14] from CSe_2 and the corresponding *ortho*-substituted primary amine in CCl_4 or benzene. 3-Methylbenzothiazole-2-selone (**14**) was prepared by nucleophilic substitution of Se on 3-methylbenzothiazolium iodide in pyridine.[15] 3-Methylbenzoxazole-2-selone (**10**) was prepared with the same procedure employed to synthesize *N*-methyloxazolidine-2-selone.[16]

Spectrophotometric Measurements.—The spectrophotometric measurements were carried out in CH_2Cl_2 (spectrophotometric grade) by recording the spectra of solutions containing different amounts of I_2 and ligand at 17 and 35 °C in the 300—500 nm interval. The choice of the reagent concentrations was made according to the above criteria.

The u.v.–visible spectrum of each adduct, from which the data for Table 1 were drawn, was obtained by subtracting from the spectrum of an appropriate solution of the reagents the absorptions of the free ligand and I_2 evaluated on the basis of the K value. On the whole, the spectral data of the adducts thus obtained are realistic, since the ε values at the wavelengths used for the calculations are very close to those calculated.

Except for (**8**) and (**14**), all the compounds show at least one isosbestic point, confirming that only a 1 : 1 molecular adduct is formed in solution. Moreover, the 1 : 1 model also fits the data well for (**8**) and (**14**).

Data Treatment.—Data analysis was carried out with a program based on a method of non-linear least-squares. The method assumes that the best values of K and ε are those that minimize the sum of the squared deviations between the experimental and the calculated points, *i.e.* $\chi^2 = \Sigma(A_c - A_s)^2/(N - 2)$, where A_c and A_s are the calculated and observed absorbances respectively and N is the number of data points. The experimental data and the details for the calculation together with the output of the program are in Supplementary Publication No. SUP 23929 (18 pp.).*

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* For details of Supplementary Publications see Notice for Authors (1984),. *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

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