

Interaction of Iodine with Some 5,5-Dimethylimidazolidines with Two Chalcogen Atoms at the 2- and 4-Positions

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The title compounds react with molecular iodine in CH_2Cl_2 solution to form 1:1 adducts. The association constants (K) have been determined from the u.v.-visible spectra of several solutions with different amounts of reagents. Competition between the two chalcogen atoms to co-ordinate I_2 is discussed and the results indicate both that molecular iodine preferentially binds the atom at the 2-position and that the donor ability increases in the order $\text{O} < \text{S} < \text{Se}$. A good correlation is found between the K values and the CNDO/S charge densities of the donor atoms.

The stability constant of reaction (1), where D is a donor



molecule and $\text{D}\cdot\text{I}_2$ its charge-transfer complex with molecular iodine, has proved to be a useful quantity which depends on the charge density of the donor atom of D.¹⁻⁴ We have employed this reaction to measure the different donor properties of sulphur and selenium in several penta-atomic rings, such as pyrrolidine,^{2,3} oxazolidine,^{2,3} thiazolidine,^{2,3} and imidazolidine^{1,3} with or without a condensed benzene ring.⁴

For this reason, we have now studied the above reaction with compounds (1)–(9) which unlike the previously investigated imidazolidine derivatives^{1,3} have (i) an additional chalcogen atom at C-4 and (ii) two methyl groups at C-5 to increase the solubility in weakly polar solvents. Since X and Y may compete in co-ordinating molecular iodine in these molecules, the aims of this work are (i) to check the donor properties of the chalcogen atom at both C-2 and C-4, and (ii) to ascertain the reciprocal influence of the two heteroatoms.

Results and Discussion

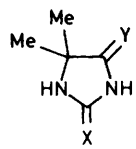
The title compounds have two heteroatoms which are able to co-ordinate with molecular iodine and as well as 1:1 complexes, 1:2 ones may be obtained. However, as shown in Figure 1 for (6) and reported in Table 1 for (2)–(9), all the charge-transfer complexes exhibit an isosbestic point between the visible band of I_2 and its blue-shifted or charge-transfer band. This fact excludes the presence of a $\text{D}\cdot 2\text{I}_2$ adduct, but not the parallel interactions of X and Y with I_2 . In fact, in the case of two simultaneous equilibria, the ratio between the two adduct concentrations must be constant and equal to the ratio between the association constants, i.e. $C_1/C_2 = K_1/K_2$. From the trivial equilibrium constant expressions, it is easy to obtain equation (2) which resembles a unique equilibrium, whose constant is

$$(K_1 + K_2) = (C_1 + C_2)/[\text{D}]\cdot[\text{I}_2] \quad (2)$$

$(K_1 + K_2)$ and whose complex concentration is $(C_1 + C_2)$.

If the K values are calculated using as experimental data the total absorbances of both complexes (see Experimental section), we can obtain the expression for the apparent molar extinction coefficient (ϵ_{ap}) in terms of the molar extinction coefficients of the two adducts, i.e. equation (3). For $\epsilon_1 + \epsilon_2$, (3) becomes $\epsilon_{\text{ap}} =$

$$\epsilon_{\text{ap}} = (\epsilon_1 K_1 + \epsilon_2 K_2)/(K_1 + K_2) \quad (3)$$

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- (1) X = Y = O
 - (2) X = S, Y = O
 - (3) X = O, Y = S
 - (4) X = Se, Y = O
 - (5) X = O, Y = Se
 - (6) X = Y = S
 - (7) X = Se, Y = S
 - (8) X = S, Y = Se
 - (9) X = Y = Se

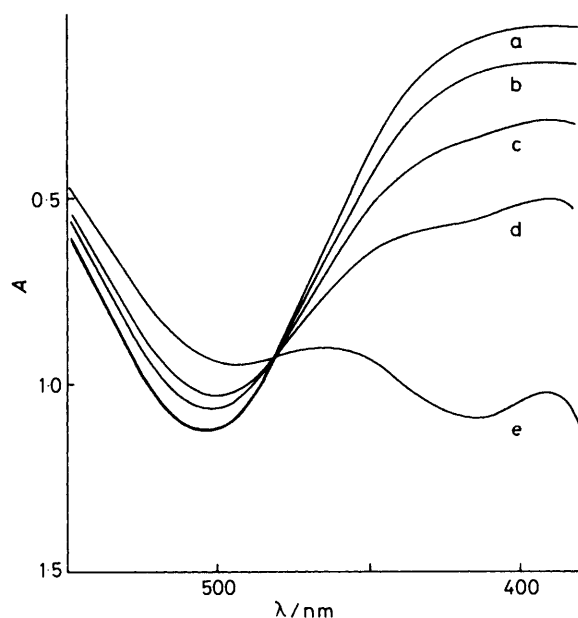


Figure 1. Isosbestic point obtained from the absorptions of the free I_2 and its adduct with (6). $[\text{I}_2]$ 1.23×10^{-3} and $[(6)]$ 1.24×10^{-4} , 6.20×10^{-4} , 1.24×10^{-3} , and 3.04×10^{-3} M for b, c, d, and e, respectively

ϵ_1 and the calculation (with a 1:1 model) gives $(K_1 + K_2)$ as association constant. If $K_1 \approx K_2$, (3) yields $\epsilon_{\text{ap}} = (\epsilon_1 + \epsilon_2)/2$, i.e. the treatment of the data mediates the ϵ values.

If one adduct is much more stable than the other, for example $\epsilon_1 K_1 \gg \epsilon_2 K_2$, ϵ_{ap} will differ from ϵ_1 by the factor $K_1/(K_1 + K_2)$.

Table 1. U.v. absorptions (nm) (log ϵ in parentheses) of the free ligands in CH_2Cl_2 and isosbestic points (nm) obtained for the reaction with I_2 in CH_2Cl_2 .

Compound	U.v. absorptions	Isosbestic point
(1)	280sh (0.22)	
(2)	266(4.34) 305(2.28)	481
(3)	274(4.20) 349(1.69) 365sh (1.66)	476
(4)	296(4.55) 349(2.71)	479
(5)	259(4.15) 302(3.48) 450sh (2.14)	485
(6)	299 (4.46) 394(1.69)	481
(7)	249sh (3.65) 288(4.16) 332(4.24)	484
(8)	252sh (3.49) 331(4.05) 471(2.21)	494
(9)	248(2.35) 318sh (2.65) 353(3.02) 485sh (2.26)	491

Table 2. CNDO/S Charge densities (a.u.) of the donor atoms and calculated molar extinction coefficients (ϵ_{ap}) at the wavelengths used for the calculation and association constants (K) of the reactions (2)—(9) with I_2 in CH_2Cl_2 solutions

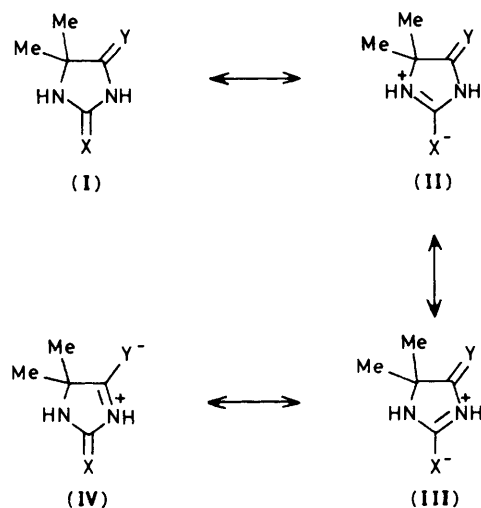
Compound	Charge density		$t/^\circ\text{C}$	λ/nm	$\epsilon_{\text{ap}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$K/\text{dm}^3 \text{ mol}^{-1}$	ΔG^a	ΔS^b
	q_x	q_y						
(1) ^c	-0.392 5	-0.365 9						
(2)	-0.408 1	-0.355 8	17	420	$2\,630 \pm 110$	$(2.91 \pm 0.22) \times 10^2$	0.10—0.77	0.90—0.13
(3) ^d			35		$2\,490 \pm 220$	$(1.30 \pm 0.17) \times 10^2$	0.20—0.88	0.80—0.07
			17	330	$45\,220 \pm 19\,300$	$(1.06 \pm 0.51) \times 10$	0.84—0.99	0.16—0.00
(4)			35		$48\,710 \pm 145\,000$	$(0.41 \pm 1.28) \times 10$	0.93—1.00	0.07—0.00
			17	400	$5\,950 \pm 160$	$(3.21 \pm 0.41) \times 10^4$	0.04—0.65	0.90—0.21
(5)			35		$5\,320 \pm 220$	$(1.22 \pm 0.16) \times 10^4$	0.04—0.47	0.96—0.37
			17	440	$4\,540 \pm 1\,190$	$(1.48 \pm 0.72) \times 10^3$	0.23—0.71	0.77—0.17
(6)			35		$4\,740 \pm 380$	$(0.63 \pm 0.29) \times 10^3$	0.22—0.84	0.78—0.09
			17	420	$3\,110 \pm 180$	$(1.99 \pm 0.21) \times 10^2$	0.27—0.90	0.73—0.05
(7)			35		$2\,980 \pm 280$	$(0.97 \pm 0.14) \times 10^2$	0.43—0.95	0.57—0.03
			17	440	$2\,850 \pm 330$	$(1.91 \pm 0.96) \times 10^4$	0.03—0.57	0.97—0.29
(8)			35		$2\,480 \pm 200$	$(0.89 \pm 0.29) \times 10^4$	0.06—0.72	0.94—0.17
			17	400	$9\,070 \pm 530$	$(5.98 \pm 0.66) \times 10^2$	0.15—0.95	0.85—0.03
(9)			35		$8\,060 \pm 520$	$(3.62 \pm 0.39) \times 10^2$	0.23—0.97	0.77—0.02
			17	450	$4\,620 \pm 380$	$(7.33 \pm 2.00) \times 10^3$	0.13—0.65	0.86—0.21
			35		$4\,460 \pm 240$	$(4.48 \pm 0.71) \times 10^3$	0.20—0.74	0.80—0.15

^a The parameter G was defined as $K^{-1} \cdot [(a + b + K^{-1})^2 - 4ab]^{-1/2}$ (where a and b are the initial concentrations of the reagents) by Carta and Crisponi.⁹ ΔG is the range of G . ^b ΔS is the range of the saturation fraction. ^c Not soluble. ^d The very narrow ΔG does not allow more reliable K and ϵ_{ap} values to be obtained. The high values of ϵ_{ap} are due to the wavelength position.

From our work with several penta-atomic rings having only one exocyclic chalcogen atom,¹⁻⁵ we have observed that the K values for equilibrium (1) strongly depend on the nature of the chalcogen, *i.e.* $\text{O} \ll \text{S} < \text{Se}$. For example, with the imidazolidin-2-one, 2-thione, and 2-selone series, the K values at 25 °C are *ca.* 10, 10⁴, and 10⁶ dm³ mol⁻¹ respectively. Because of this, it is very probable that in (2)—(5) the donor atom is only sulphur or selenium and that we have the $\epsilon_1 K_1 \gg \epsilon_2 K_2$ case, which gives calculated K and ϵ values of the more stable adduct.* These values are reported in Table 2 for 17 and 35 °C. The comparison between the K values obtained for (2) and (3) shows that the sulphur at C-2 is a better donor than that at C-4. The same is true for (4) and (5), which, as expected, form more stable adducts than the corresponding sulphur derivatives. The higher donor ability of sulphur or selenium at C-2 with respect to C-4 was experimentally tested by treating (2)—(5) with methyl iodide. Compounds (2) and (4) react to yield S- or Se-methiodide, while (3) and (5) do not. Compound (6) reacts with MeI giving methylation on sulphur at C-2, thus confirming that

this position is more nucleophilic than sulphur at C-4. The K values obtained for this compound are similar to those obtained for (2) and (3) and closer to those for (2). Although the ratio of the K values of (2) and (3) is *ca.* 30, the competition of the two sulphur atoms for co-ordination should be effective for (6). However, if we assume that a similar ratio of *ca.* 30 is reached in (6), its K value is due mainly to the adduct bonded through X. On the other hand, the lower K values of (6) compared with those of (2) can be explained in terms of electron withdrawal by the sulphur at C-4 being higher than that of oxygen. In terms of the resonance theory (Scheme) this means that the importance of the zwitterions increases on passing from oxygen to sulphur and selenium, as proved for analogous molecules.^{6,7}

By considering the K values of (9), we again found that these are between those of (4) and (5). As discussed above, it is



Scheme.

* Although the K values for (3) are of the same order of those obtained for imidazolidin-2-one,⁵ the presence of a sulphur at C-4 lowers greatly the donor ability of the oxygen at C-2. Furthermore, the ϵ values of the two possible adducts are very different at 330 nm, since the charge-transfer band for the interaction of I_2 with oxygen falls below 300 nm, whereas that with sulphur is at *ca.* 300 nm.

possible that the selenium bonded to C-2 is mainly responsible for the K values, and that the lower values of (9) with respect to those of (4) are due to the fact that the contribution of the

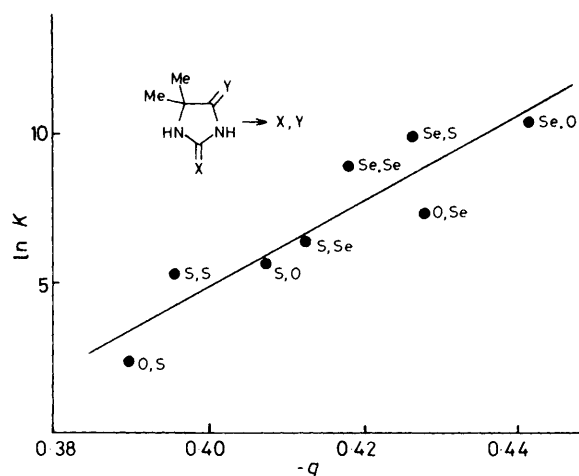


Figure 2. Association constants ($\ln K$) of (2)–(9) versus the charge densities (a.u.) of the donor atoms. The charges are those referred to the more negative X or Y. The correlation coefficient $r = 0.908$

resonant form (IV) is higher in the presence of $Y = \text{Se}$ than in presence of $Y = \text{O}$.

Compound (7) has K values slightly lower than those of (4) due to the different effect of sulphur and oxygen bonded to C-4 on the donor properties of selenium on C-2. On the other hand, the donor properties of the sulphur bonded to C-4 in (3) are very low and we expect it to decrease further, on substituting the oxygen on C-2 with selenium, according to the previous discussion. Consequently, in (7) we believe that the co-ordinative bond occurs only through the selenium atom.

The results for compound (8) are more complex. Here the donor properties of sulphur bonded to C-2 are slightly lower than those of selenium at C-4, and in solution there should be competition between them in forming co-ordinative bonds with I_2 . Hence, in this case the evaluated K could be considered as the sum of the K values of the two equilibria, i.e. ($K_1 + K_2$), even if their values indicate that selenium is the main donor atom. Consequently, the calculated values can be interpreted as in equation (3).

However, considering that methylation in this series of compounds always occurs on $>\text{C}=\text{X}$ and that (8) does not react with MeI , the stability constant for the sulphur adduct must be much lower than the 1.99×10^2 (at 17°C) evaluated for (6), which reacts with MeI .

In Figure 2, the $\ln K$ values at 17°C are reported against the charge densities of X or Y, calculated from CNDO/S. For each compound the charge used in this correlation is the more negative of those reported in Table 2. The good correlation indicates that the interaction between these ligands with molecular iodine occurs mainly through the more negatively charged X or Y atom.

Experimental

The substances were prepared and purified according to the literature.⁸

Spectrophotometric measurements were carried out in CH_2Cl_2 solutions as previously described,⁴ by selecting the reagent concentrations according to the suggestions of Carta and Crisponi,⁹ i.e. by making the range of G (see Table 2) or that of the saturation fractions as large as possible. The realized ranges of G and s are reported in the two last columns of Table 2.

The data treatment was carried out using a non-linear least-squares method.⁹ The absorbance values (A_s) used for the calculation were taken from equation (4) where A_s^0 is the

$$A_s = A_s^0 - \epsilon_{\text{I}_2}[\text{I}_2]_0 - \epsilon_{\text{D}}[\text{D}]_0 \quad (4)$$

absorbance, ϵ_{I_2} and ϵ_{D} the molar extinction coefficients of I_2 and the donor respectively, and $[\text{I}_2]_0$ and $[\text{D}]_0$ the initial molar concentrations. In the case of two parallel 1:1 equilibria (adducts via X and Y), the absorbance is due to both complexes, i.e. $A_s = \epsilon_1 C_1 + \epsilon_2 C_2$.

By introducing the absorbance A_s instead of ($C_1 + C_2$) in equation (2), we obtain equation (3). Hence, the calculation gives ($K_1 + K_2$)⁸ as equilibrium constant, and ϵ_{ap} as molar extinction coefficient of the mixture of the two adducts [see Supplementary Publication No. SUP 56212 (10 pp.)* for data].

Quantum mechanical calculations were performed on a UNIVAC 1100 computer, using the CNDO/SHIFT/UV program (QCPE no. 382), with CNDO/S parametrization.

The structural parameters were transferred from X-ray data for *N*,5,5-trimethyloxazolidine-2,4-dione¹⁰ for the methyl groups bonded to C-5 and for 2-thiohydantoin¹¹ for the hydantoin skeleton. The C–O bond lengths were assumed to be 1.218¹² and 1.225 Å¹¹ for C-2 and C-4, respectively, while the C–S¹¹ and C–Se¹³ bond lengths were 1.65 and 1.82 Å, respectively, for both positions.

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* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.