

Electronic absorption spectra of selenocarbonyl and thiocarbonyl compounds

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Abstract. Electronic absorption spectra of a variety of thiocarbonyl and selenocarbonyl compounds have been compared to point out their similarities. Interesting correlations between the absorption maxima and electronegativities of substituents in both the seleno- and thio-carbonyl compounds have been reported.

Keywords. Electronic absorption spectra; selenocarbonyl; thiocarbonyl.

1. Introduction

Electronic transitions of carbonyl compounds have been well understood for some years (Jaffe and Orchin 1962; Rao 1975). Electronic transitions of thiocarbonyl compounds show features generally similar to those of the carbonyl compounds, although there are some uncertainties with regard to band assignments in some of the compounds, particularly those where a nitrogen atom is linked to the thiocarbonyl group (Janssen 1960; Rao *et al* 1961). Selenocarbonyl compounds are known to exhibit $n-\pi^*$ transitions at longer wavelengths than the corresponding thiocarbonyl compounds and the features of their electronic spectra can be compared to those of the thiocarbonyl compounds (Shankaranarayana 1970). It was considered interesting to closely examine the similarities between the electronic absorption spectra of the selenocarbonyl and the thiocarbonyl groups in several related series of compounds. This paper presents our results on such a comparative study along with correlations of the absorption maxima with the electronegativities of substituents.

2. Experimental

2.1. Derivatives of diselenocarbonic acid

Potassium ethyl diselanoxanthate (Potassium O-ethyl diselenocarbonate) was prepared by reacting potassium ethanolate and carbondiselenide (Grimmand and

Motzger 1936). Se-carboxy-methylesters of O-alkyl diselenocarbonic acid, {[(alkoxy)selenocarbonyl] seleno} acetic acid, $RO C(Se) Se CH_2COOH$, in which, $R = C_2H_5$, $n-C_3H_7$, $i-C_3H_7$ were prepared by standard procedures (Jensen *et al* 1970). Carboxymethyl S-isopropyl and carboxymethyl S-isobutyl diselenocarbonates {[(alkylthio) selenocarbonyl] seleno} acetic acid, $RS C(Se) Se CH_2COOH$, were prepared according to the procedure of Jensen and Anthoni (1970).

2.2. Derivatives of diselenocarbamic acid

Sodium N,N-diethyl diselenocarbamate was prepared by the procedure of Rosenbaum *et al* (1963). Carboxymethyl N,N-diethyl and N,N-dipropyldiselenocarbamate and carboxymethyl piperidine were prepared by known procedure (Shankaranarayana 1970). All other selenium compounds studied were available in the pure state. All the solvents used for absorption spectral studies were purified and freshly distilled.

Electronic absorption spectra were recorded with a Perkin Elmer (Model 137) spectrophotometer using 1 cm fused quartz matched cells at room temperature. Typical data on the absorption maxima (λ_{max}) and intensities at peak maxima ($\log \epsilon_{max}$) are shown in tables 1 and 2.

3. Results and discussion

Data on the electronic absorption spectra of a typical set of selenocarbonyl compounds with the $C=Se$ group linked to atoms of different electronegativities are presented in table 1. Data on the corresponding set of thiocarbonyl compounds are given in table 2. It is clearly seen that the absorption bands of selenocarbonyl compounds extend to considerably longer wavelengths than those of thiocarbonyl compounds as expected on the basis of the lower ionisation energy of selenium compared to sulphur. The bands in the electronic spectra of selenocarbonyl and thiocarbonyl compounds can be classified as follows:

Band I : All the compounds containing $C=Se$ or $C=S$ group show a band of relatively low intensity ($\log \epsilon < 2.3$) at the longest wavelength band. This band, designated as band I, in tables 1 and 2, show characteristic blue shifts in polar solvents and are undoubtedly due to the $n-\pi^*$ transitions of the $C=Se$ or $C=S$ groups. We find the intensity of the $n-\pi^*$ transition of the $C=Se$ group to be generally greater than that of the $C=S$ group. The blue shift of the transition of the $C=Se$ group in acetonitrile solvent is around 543 cm^{-1} (with respect to cyclohexane solvent). The corresponding value for the $C=S$ groups is 237 cm^{-1} .

Bands II and III : All the compounds show an intense band ($\log \epsilon \sim 4$) after the $n-\pi^*$ transition and this band shows a slight red shift in polar solvents. This band, designated as band III in tables 1 and 2, can be considered to be due to the $\pi-\pi^*$ transition of the $C=Se$ or the $C=S$ group. In diseleno- and dithio-carbamates, we see another intense band ($\log \epsilon \sim 4$) between bands I and III (see tables 1 and 2). We shall designate this band as band II to be in conformity with the literature (Janssen 1960; Shankaranarayana 1970). Band II shows slight blue shifts

in polar solvents. While one may be tempted to assign this to an $n-\sigma^*$ transition (Rao 1975), arguments against it would be as follows. All thiocarbonyl and selenocarbonyl compounds do not show this band. The position of band II, in fact, fits in better with the data on other compounds if it is assigned to a $\pi-\pi^*$ transition, as will be shown later. The position of band II is similar to that of band III in a selenoamide or thioamide (see tables 1 and 2). We may consider band II to originate from the extended double bond $N=C=Se$ or $N=C=S$, resulting from the interaction of the lone pair on the nitrogen; it is known that the C-N bond order in such amide-type derivatives is considerably larger than unity. The solvent blue shift of band II probably arises because of the interaction with the nitrogen lone pair in the ground state affecting in turn the $N=C=Se(S)$ bond. We shall therefore assign band II to a $\pi_N-\pi^*$ transition. This assignment will be justified further when we discuss the correlation of the positions of absorption maxima with electronegativities of substituents.

Band IV: We find this band only in those compounds containing C(Se)Se or C(S)S groups (tables 1 and 2). The band is intense ($\log \epsilon \sim 4$) and essentially solvent insensitive. We could consider this to be related to the excitation of the Se lone pair in the C-Se bond.

The correspondence between the electronic absorption spectra of selenocarbonyl and thiocarbonyl derivatives is illustrated in figures 1 and 2, where we have plotted the absorption maxima of the selenocarbonyl compounds against the absorption maxima of the corresponding bands of the thiocarbonyl compounds. Both the $n-\pi^*$ and $\pi-\pi^*$ transitions (bands I and III) show similar shifts when we go from C=S to C=Se as we see from the slopes of the plots in figures 1 and 2. Band II of the diseleno- and dithio-carbamate derivatives fall in line with the band III (figure 1) indicating the common origin of the bands II and III in these compounds. Band IV, however, shows a different slope (figure 1) indicating that its origin is different.

Table 1. Electronic absorption spectra of typical selenocarbonyl compounds^a.

Compound	X, Y	Band I	Band III	Band IV
HOOCCH ₂ SeC(Se)SeCH ₂ COOH	Se Se	545 (1.96)
<i>n</i> -C ₂ H ₅ SC(Se)SeCH ₂ COOH	S Se	541 (1.92)	357 (3.87)	325 (4.00)
C ₂ H ₅ OC(Se)SeCH ₂ COOH	O Se	433 (2.09)	319 (4.33)	243 (4.34)
(C ₂ H ₅) ₂ NC(Se)SeCH ₂ COOH	N Se	400 (2.20)	265 (4.04)	255 (4.06)
			(317) (3.96)	
CH ₃ C(Se)NH ₂	C N	..	294
C ₂ H ₅ OC(Se)OC ₂ H ₅	O O	350 (1.72)	256 (4.01)	..
<i>n</i> -C ₂ H ₅ OC(Se)NH ₂	O N	325 (2.26)	274 (3.94)	..
(CH ₃) ₂ NC(Se)NH ₂	N N	..	273 (4.35)	..

^a X and Y are elements directly linked to the C=Se group. Log ϵ values are given in parenthesis and λ_{\max} values are in nm. The λ_{\max} value in parenthesis is the so-called band II (solvent; saturated hydrocarbon).

Table 2. Electronic absorption spectra of typical thiocarbonyl compounds^a.

Compound	X, Y	Band I	Band III	Band IV
CH ₃ SC(S)SCH ₃	S S	429 (1.45)	303 (4.21)	238 (3.55)
CH ₃ OC(S)SC ₂ H ₅	O S	357 (1.72)	278 (4.12)	221 (3.94)
(CH ₃) ₂ NC(S)SCH ₃	N S	343 (1.71)	246 (3.92)	224 (3.92)
			(277) (4.02)	..
(CH ₃) ₂ NC(S)CH ₃	C N	365 (1.61)	272 (4.17)	..
C ₂ H ₅ OC(S)OC ₂ H ₅	O O	303 (1.72)	228 (3.68)	..
CH ₃ OC(S)N(CH ₃) ₂	O N	286 (1.82)	247 (4.02)	..
(CH ₃) ₂ NC(S)NHCH ₃	N N	295 ..	211 (4.11)	..
			(251) (4.09)	..

^a X and Y are elements directly linked to the C=S group. log ϵ values are given in parenthesis and λ_{\max} values are in nm. The λ_{\max} value in parenthesis is the so-called band II (solvent: saturated hydrocarbon).

It has been found instructive to relate the positions of the $n-\pi^*$ bands of the thiocarbonyl derivatives with the electronegativities of adjacent atoms (Rao *et al* 1961). In figure 3, we have plotted the λ_{\max} values of bands I and III of compounds containing XC(Se)Se and XC(S)S groups against the electronegativity of X. There is a large decrease in the λ_{\max} of $n-\pi^*$ transition (band I) when X is a nitrogen atom indicating that there is more effective electron donation from an adjacent nitrogen atom than from oxygen, sulphur or selenium. That is, the λ_{\max} of band I varies in the order $\text{SCSe}_2 > \text{OCSe}_2^- > \text{NCSe}_2^-$ (resembling $\text{SCS}_2 > \text{OCS}_2 > \text{NCS}_2$). This behaviour is also exhibited by the CSe_2^- and CS_2^- anions. It is known that the $n-\pi^*$ transitions are shifted to lower wavelengths by electron donating groups (Rao 1975). Band III λ_{\max} values show a large decrease when X is nitrogen (in carbamate derivatives X = N), and again increase when X is (the more electronegative) oxygen. However, if we plot the λ_{\max} of band II (of carbamates) the correlation becomes smooth. This is justified by the correlations of λ_{\max} values with electronegativity shown in figure 4. In figure 4a where we have plotted λ_{\max} values of bands I and III in compounds containing XC(S)N, XC(Se)N groups against the electronegativity of X, we get a meaningful variation of λ_{\max} with electronegativity of the adjacent atom, only if we plot the position of band II, in the case of carbamate derivatives (X=S or Se); the λ_{\max} values of band III of these derivatives as listed in tables 1 and 2 are too low to be meaningful, values which are much lower than the values in compounds with X = N or O. That there should be a smooth decreasing relation between λ_{\max} of band III and electronegativity of the adjoining atoms is also seen in figure 4b where we have shown the data for compounds containing XC(S)O or XC(Se)O groups. These correlations seem to justify the nature of assignment for band II discussed earlier. The $n-\pi^*$ transition bands (band I) shows marked lowering when X = N in figure 4b; the curve for band I is, however, smooth for compounds containing XC(S)N or XC(Se)N groups (figure 4a). Once there is one nitrogen atom directly linked to the C=Se or C=S groups, there is no

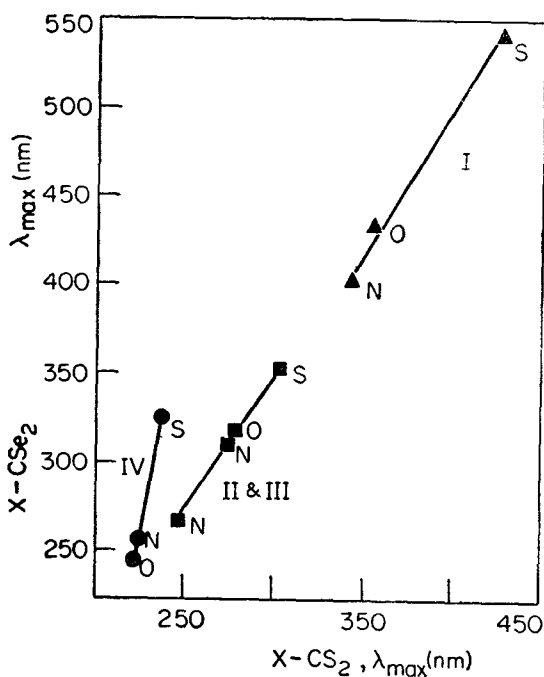


Figure 1. Correlation of the absorption maxima (bands I to IV) in the electronic spectra of diselenocarbamic acid derivatives with those of the corresponding dithio-derivatives.

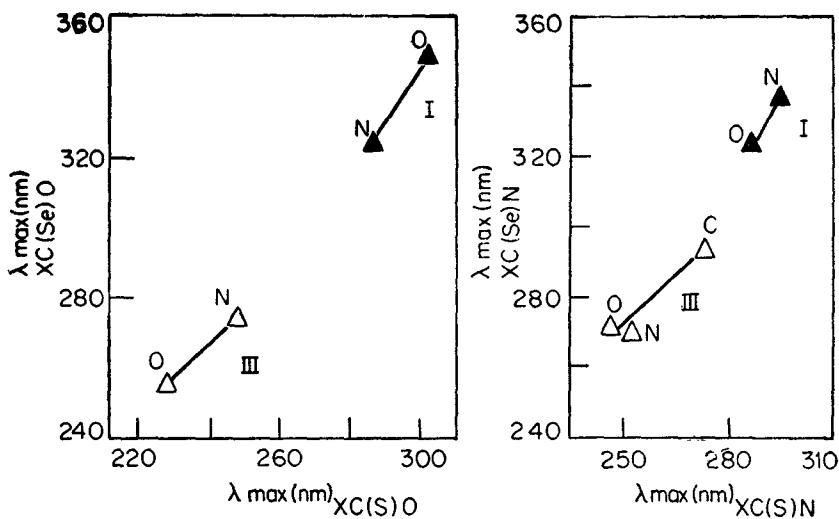


Figure 2. Correlation of the absorption maxima (bands I and III) in the electronic spectra of selenocarbamates, selenoureas, and other derivatives containing XC(Se)O or XC(Se)N linkages with those of the corresponding thio derivatives (containing XC(S)O or XC(S)N linkages).

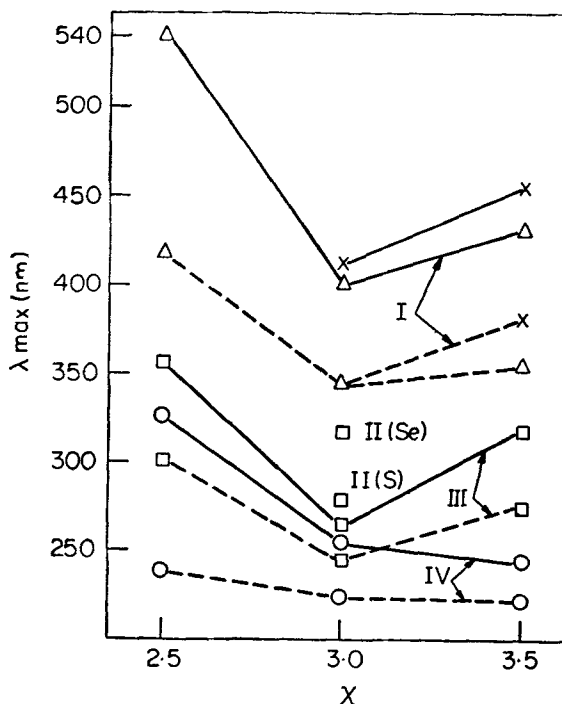


Figure 3. Correlation of the absorption maxima (bands I, III and IV) in the electronic spectra of diseleno- and dithio-derivatives containing XC(Se)Se and XC(S)S linkages respectively with the electronegativity of X. Full lines correspond to diseleno-derivatives and dotted lines to dithio-derivatives. The two sets of points designated by a 'x' sign correspond to anions containing XCSe₂⁻ or XCS₂⁻ groups. We have shown positions of band II for the diseleno- and dithio-carbamates.

anomalous decrease, whatever be the other adjacent atom (including another nitrogen).

In figure 5, we have attempted a more general correlation of bands I and III in selenocarbonyl and thiocarbonyl derivatives with the sum of the electronegativities of the two adjacent atoms. We see that these λ_{\max} values show a decreasing trend with increasing electronegativity. This correlation is interesting and again supports our earlier assignment of band II. The sum of electronegativities of adjacent atoms (X and Y) would be the same when they are N and S or C and N; if we take band III listed in table 2 for a dithiocarbamate when X = N and Y = S, it would be far too low (246 nm) compared to λ_{\max} of the thioamide where X = C and Y = N (272 nm); band II of the dithiocarbamate is, however, 277 nm and is readily correlated. Accordingly, we have shown band II positions for the carbamate derivatives in figure 5.

The similar correlations found for the electronic absorption spectra of selenocarbonyl and thiocarbonyl derivatives with electronegativities of adjacent atoms as well as exact correspondence observed between like bands (of the same origin) reinforce the common band assignments made in this paper for the two series of compounds and indicate that the broad generalisations regarding substituent and

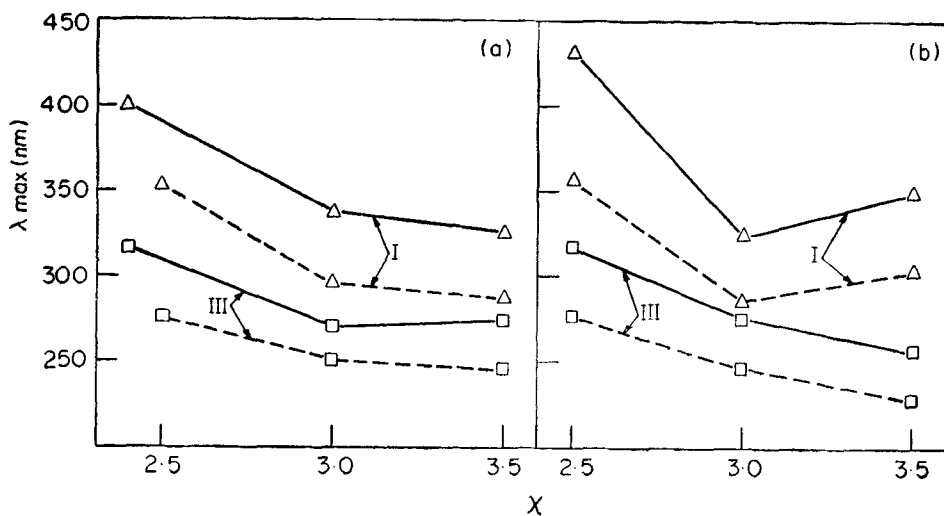


Figure 4. (a) Correlation of absorption maxima (bands I and III) of seleno- and thio-derivatives containing XC(Se)N and XC(S)N linkages respectively with the electronegativity of X. Positions of band II have actually been plotted in the case of diseleno- and dithio-carbamates. (b) Correlation of the absorption maxima (bands I and III) of seleno- and thio-derivatives containing XC(Se)O and XC(S)O linkages respectively with the electronegativity of X. In both (a) and (b), full lines correspond to seleno-derivatives and dashed lines to thio-derivatives.

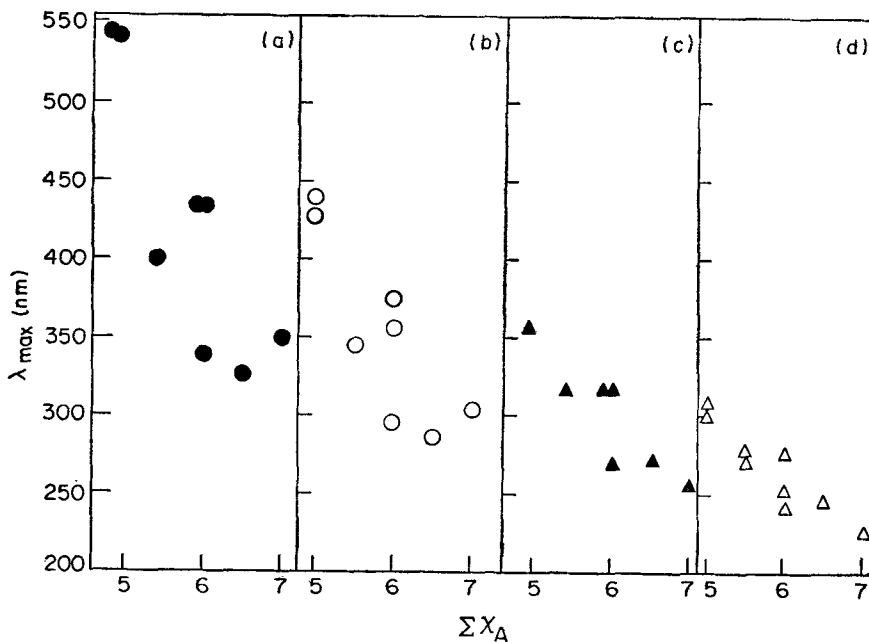


Figure 5. Correlation of absorption maxima of selenocarbonyl and thiocarbonyl derivatives with the sum of the electronegativities of adjacent atoms. (a) Compounds with XC(Se)Se, XC(Se)O or XC(Se)N grouping (band I). (b) Compounds with XC(S)S, XC(S)O or XC(S)N grouping (band I). (c) Compounds with XC(Se)Se, XC(Se)O or XC(Se)N grouping (band III; II in the last case). (d) Compounds with XC(S)S, XC(S)O or XC(S)N grouping (band III; II in the last case).

solvent effects on the electronic transitions of the carbonyl group hold for thio- and seleno-carbonyl groups as well.

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