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Ultraviolet Absorption Spectra of Saturated Disulphides and Diselenides

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Submitted in honour of the sixtieth birthday of our teacher, Professor *Arne Fredga*

The ultraviolet absorption spectra of a number of saturated aliphatic disulphides and diselenides have been discussed. Special attention is paid to the following problems: (1) The nature of the first absorption band, (2) The red-shift found in small cyclic systems, (3) The effect of unsymmetrical substitution and (4) The interactions found between divalent sulphur atoms and carbonyl- and carboxyl-groups.

The first absorption band originates in a transition from the highest π-orbital (formed by combination of the lonepair atomic-orbitals) to the antibonding σ-orbital in the S—S or Se—Se bond.

The red shift found in small cyclic molecules is explained by the variation of the orbital energy in the highest π-orbital with the dihedral angle of the C—S—S—C group. Unsymmetrical disulphides show only one absorption peak as do symmetrical molecules. This is also true for the highly unsymmetrical molecules containing the Se—S bond.

The interaction between divalent sulphur atoms and carbonyl- or carboxyl-groups is complex. Two different mechanisms can be distinguished. The first results in a perturbation of the $n \rightarrow \pi^*$ transition, and the second is a charge-transfer mechanism.

Many measurements of UV absorption spectra of disulphides and related compounds have been reported, and the interpretations given almost exceed the number of spectra. Owing to the increasing interest in disulphide chemistry it seems justified to collect a number of representative spectra together with their recent interpretations. The present review is, however, incomplete and special reference is paid to the work performed in this field by the Uppsala school. We will deal exclusively with saturated disulphides and diselenides, defined as molecules containing the group:

$$-\overset{|}{\underset{|}{C}}-S-S-\overset{|}{\underset{|}{C}}- \quad \text{or} \quad -\overset{|}{\underset{|}{C}}-Se-Se-\overset{|}{\underset{|}{C}}-$$

The absorption due to these chromophors is not as simple as at first it might appear. The first absorption peak (*i.e.*, that occurring at longest wavelengths) can vary from about 230 to 370 mμ for disulphides depending on the molecular environment.

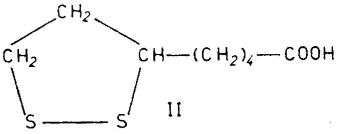
It has been found very convenient to compare the disulphide spectra with the spectra of the corresponding diselenides. The diselenides show very similar spectra but they are found at longer wavelengths and this facilitates their study by means of simple commercial instruments. In some instances the disulphides have the first absorption peak near the borderline of the vacuum-ultraviolet region. Ditellurides are even more highly coloured than the diselenides, but their preparation is somewhat more difficult. In Fig. 1 the spectra of some simple compounds illustrate these findings. The three compounds referred to are colourless, yellow and deep-red, respectively. The large variations which may occur in the absorption curves are exemplified in Fig. 2, where the spectra of di-*t*-butyldisulphide (I), 6,8-thioctic acid (II) and 1α,5α-epidithioandrostane-3α,17β-diol (III) are given.

Already in 1936 Fredga[1] pointed out that among the acids with the general formula (IV) those with $n \neq 0$ were colourless whereas the acid with $n = 0$ was yellow, as are other diselenides. The diselenide group accordingly appeared to constitute a special chromophoric system. The spectra of some of the acids cited have now been measured and are given in Fig. 3.

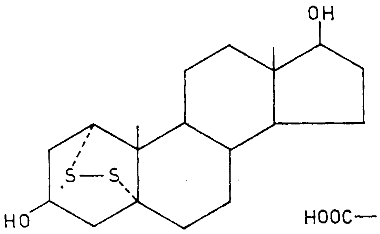
Similar results were reported earlier for sulphur compounds. According to Ley and Arends[2], a maximum at about 250 mμ is characteristic of the disulphide group. In monosulphides with the exception of a few cases[3] the first absorption peak is always found below 250 mμ. It is true that the results quoted so far do not prove the existence of a new type of transition for the disulphides as compared with the monosulphides. They might be attributable instead to displacements of the absorption bands towards longer wavelengths. There are, however, many examples which support the idea of a characteristic absorption peak for the disulphides or diselenides. In Fig. 4, the spectra of 1,3-dithiolane (V) and 1,2-dithiolane (VI) are compared. Although (VI) does not show any

$(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$

I



II



III

$HOOC{-}CH_2{-}Se{-}(CH_2)_n{-}Se{-}CH_2{-}COOH$

IV

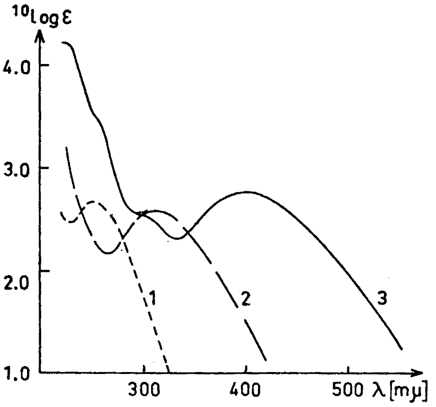


Fig. 1. UV-absorption of: 1. Dipropyl disulphide. 2. Dibutyl diselenide 3. Dibutyl ditelluride.

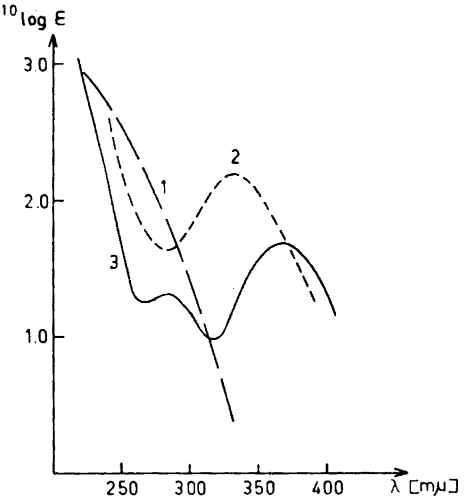


Fig. 2. UV-absorption of: 1. Di-*t*-butyl disulphide (I). 2. 6,8-Thioctic acid (II). 3. 1*a*, 5*a* - Epidithioandrostane - 3*a*, 17*β* - diol (III).

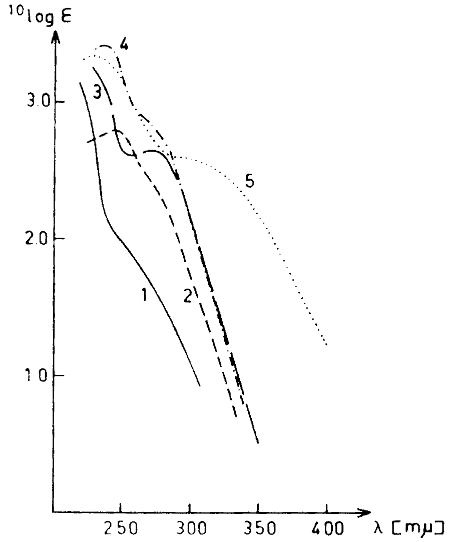


Fig. 3. UV-absorption of: 1. Ethylbutylselenide. 2. Selenium-diacetic acid ($HOOC-CH_2-Se-CH_2-COOH$). 3. Trimethylene-bis-selenium-acetic acid (IV with n = 3). 4. Methylene - bis - selenium-acetic acid (IV with n=1). 5. Diselenium-diacetic acid (IV with n = 0).

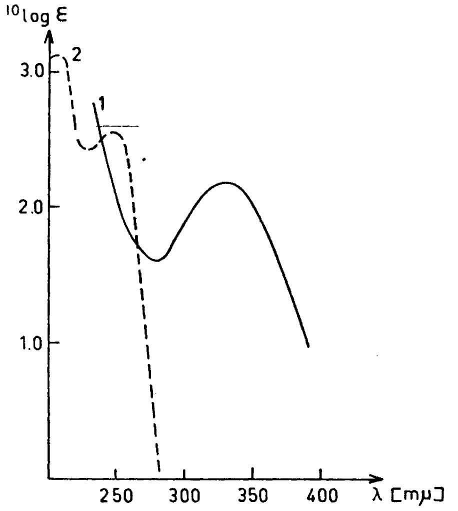


Fig. 4. UV-absorption of: 1. 1,2-Dithiolane (VI). 2. 1,3-Dithiolane (V).

maxima in and below the 250 mμ region, the extinction coefficient is rather high in this region. This indicates that absorption bands may occur at these wavelengths, as is found for (V). The peak at 330 mμ for the disulphide is, however, very pronounced and specific.

In the next paragraph it will be shown that there is also theoretical evidence for the occurrence of a specific absorption peak for disulphides and diselenides. In this connection the important work of Whitney and Calvin[4] on the quantum yield in photolysis with monochromatic light is noteworthy. A quantum yield of almost unity indicates a repulsive upper state, and there is strong evidence for the formation of R—S radicals. This implies that the electronic configuration in the S—S bond changes in the transition.

The nature of the first absorption band. Since in all the molecules considered in this paper the disulphide (or diselenide) group is surrounded by saturated carbon atoms, and the absorption occurs in a region very different from that of hydrocarbon spectra, to a first approximation we can treat the disulphide group as an isolated diatomic unit. Of course this cannot be done if it is part of a conjugated system. According to Pauling[5] the bonds formed by divalent sulphur atoms involve mainly p-orbitals. The two lone-pairs on each sulphur atom therefore occupy an s- and a p-orbital. According to Bergson[6] the simple molecular-orbital theory indicates that the two highest occupied orbitals should be the bonding and antibonding π-orbitals formed by linear combination of the non-bonding 3p$_z$-atomic orbitals. The lowest unoccupied orbital

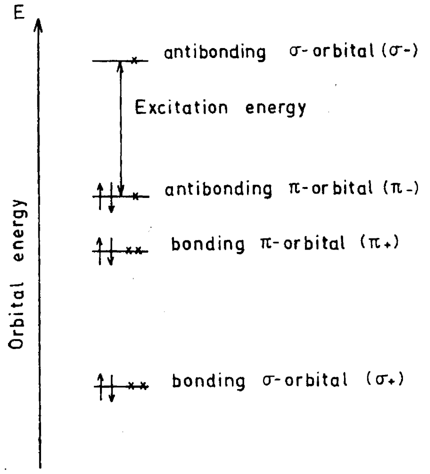


Fig. 5. Schematic representation of molecular-orbital energy levels in a disulphide.

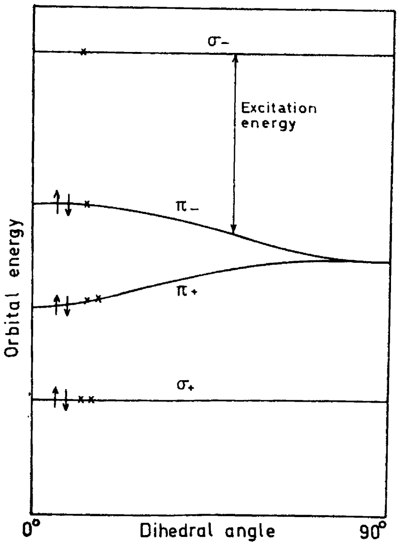


Fig. 6. Orbital energies as a function of the dihedral angle for a symmetrical disulphide. ↑ denotes electrons in the ground state and × electrons in the first excited state. The molecular orbitals have been formed from non-hydridized atomic orbitals.

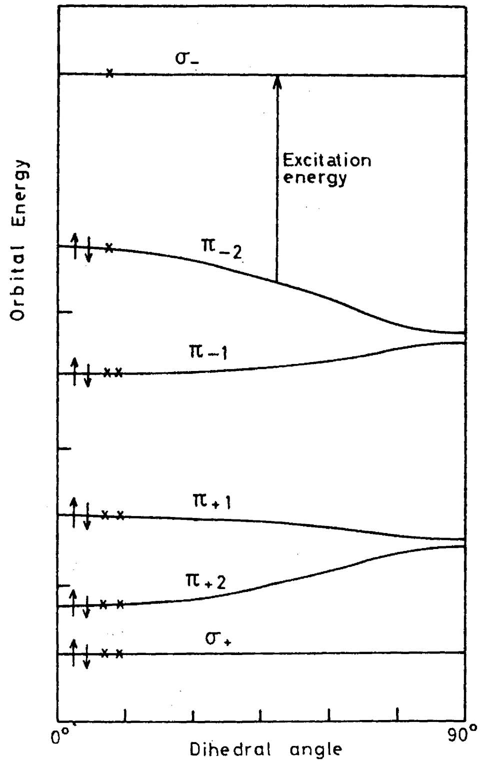


Fig. 7. Orbital energies as a function of the dihedral angle when sp^3-hybridized atomic orbitals have been used.

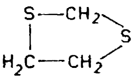
should be the antibonding σ-orbital between the sulphur atoms (*cf.* Fig. 5). Accordingly the first electronic transition should be a jump from the antibonding π-orbital to the antibonding σ-orbital. The variation of the orbital energies with the dihedral angle of the disulphide group (Fig. 6) has been studied by Bergson[6,7]. These variations account for the stable skew conformation of the disulphide group in the ground state (dihedral angle usually about 90°) and also for the red shift in UV-spectra when the molecule is forced into a conformation with a smaller dihedral angle. This is the case with the five-membered rings for example. According to Foss[8], the dihedral angle in 1,2-dithiolane-4-carboxylic acid is 27°. This model also explains the fission of the disulphide bond upon irradiation[4,9].

The most serious objection to this simple picture is that unhybridized atomic orbitals have been used as a starting point. In reality the lone-pairs often occupy orbitals which are more like sp^3-hybrids. However, Bergson[7] has treated the problem using sp^3-hybridized atomic orbitals and this leads to a very similar picture for the orbitals in question (Fig. 7).

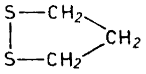
THE SPECTRA OF UNSUBSTITUTED DISULPHIDES AND DISELENIDES

Ley and Arends[2] seem to be the first to have assigned an absorption peak at about 250 mμ to the presence of the S—S group. Since then several investigators have confirmed this observation. In this connection the extensive work of Koch [10] and Brandt, Emeleus and Hazeldine [11] and also Baer and Carmack [12] may be mentioned. A characteristic absorption curve of this type has already been shown in Fig. 1. The only exceptional case seems to have been di-*t*-butyldisulphide (Fig. 2), where no maximum is present. A phenomenological explanation was advanced by Bergson [13]. The absorption maximum was shown to be displaced to progressive shorter wavelengths in the series $(CH_3)_2S_2$ (λ_{max} = 254.5 mμ), $(C_2H_5)_2S_2$ (λ_{max} = 251.5 mμ) and $(i\text{-}C_3H_7)_2S_2$ (λ_{max} = 245.0 mμ). By extrapolation the peak for $(t\text{-}C_4H_9)_2S_2$ would be expected to occur at about 230 mμ. At such small wavelengths this absorption band must be so strongly overlapped by the higher-intensity bands which always occur in this region, that no maximum is detectable. This interpretation was confirmed by a study of the corresponding diselenide [13]. As mentioned in the introduction (*cf.* Fig. 1) the diselenides show absorption curves very similar to those of the corresponding disulphides, but are more easily studied since their first absorption peak occurs at longer wavelengths. For $(CH_3)_2Se_2$, $(C_2H_5)_2Se_2$, $(i\text{-}C_3H_7)_2Se_2$ and $(t\text{-}C_4H_9)_2Se_2$ the maximum is found at 316, 312, 305, and 286 mμ, respectively. Hyperconjugation is certainly of importance in determining the trend [13].

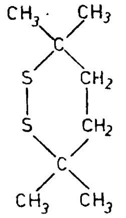
The maximum for the disulphides mentioned above is thus found between 230 and 255 mμ, and for the diselenides between 286 and 316 mμ. Consequently, the observations made by Calvin and his co-workers [14] in 1954 constitute a great advance. They reported that 1,2-dithiolane (VI) and its derivative, 6,8-thioctic acid (II), had an absorption peak at 330 mμ, and that the peak at 250 mμ was absent (*cf.* Figs. 2 and 4). Although his interpretation that this red-shift originated in ring strain is not wholy true [6,7,9,15] Calvin was the first



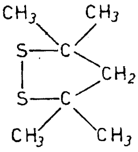
V



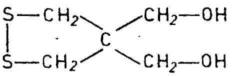
VI



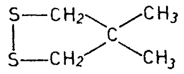
VII



VIII



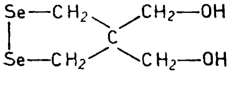
IX



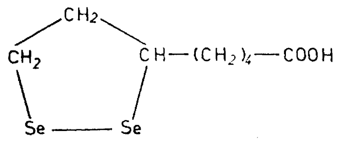
X

$C_2H_5-Se-Se-C_2H_5$

XI



XII



XIII

to point out the relationship between ring size and the position of the first absorption peak. Thus for a seven-membered ring (4,8-thioctic acid) he found the peak at 259 mμ (the same value is also found in 1,2-dithiepan-5-carboxylic acid[16] and is almost that of a noncyclic compound), for a six-membered ring at 286 mμ, and for the five-membered ring at 330 mμ as already stated. He also realized that the dihedral angle of the disulphide group decreased as the number of atoms in the ring decreased. The real cause of the redshift is fully explained from Bergson's theory of the variation of the orbital energies with the dihedral angle (see Figs. 6 and 7).

Schotte[17] investigated some 4-substituted 1,2-dithiolane derivatives prepared by Backer and his co-workers[18], and confirmed the presence of an absorption peak in the 330 mμ region. Some of these spectra are shown in Fig. 8. Claeson[19] prepared and studied the methyl-substituted 5- and 6-membered rings (VII) and (VIII). In the six-membered ring the methyl groups cause an hypsochromic shift as expected. However, by comparison with the unsubstituted ring, methyl substitution in the fivemembered ring results in a red-shift. Evidently, the factors which determine the hypsochromic shift associated with methylsubstitution in non-cyclic systems do not operate in the fivemembered ring. The spectra of (VII) and (VIII) are given in Fig. 9.

A disulphide with an absorption maximum at still longer wavelengths was recently investigated by Bergson and co-workers[20]. This was the steroid with formula (III), for which the spectrum has already been given in Fig. 2. We think that the exceptionally low excitation energy originates in the almost planar conformation of the molecule and in the large S—S distance.

Before concluding this paragraph it remains to mention the bathochromic shift found for diselenides in which the diselenide group is a part of a small ring. The six-membered ring compound 1,2-diselenane has its maximum at 365 mμ and the five-membered 1,2-diselenolane at 444 mμ[9]. In Fig. 10 some examples of diselenide absorption spectra are given. It is true that the examples given of the five-membered rings are not unsubstituted compounds, but the substituents are so far removed from the diselenide group that they cannot influence the first absorption peak.

Some unsymmetrical molecules. The study of unsymmetrical disulphides or diselenides where the two sulphur (or selenium) atoms are not equivalent is of great theoretical importance. Our first studies on unsymmetrical carboxylic substituted disulphides indicated the presence of two absorption peaks which at first we attributed to the unsymmetrical arrangement. However, such an interpretation is not in agreement with our theory of the nature of the absorption band[7,21]. Since the effect of carboxylic groups on the disulphide spectra is complex, however, it was desirable to study simpler unsymmetrical molecules.

Schotte[22] prepared and studied some trichloromethylalkyl disulphides, the spectra of which are given in Fig. 11. No definite absorption peaks are shown by these molecules so that no answer to the asymmetry problem could be obtained from them. The spectra of the unsymmetrical dialkyl disulphides given in Fig. 12 show only one peak, but here the difference between the substitutents is slight.

The thiolselenenates (R—Se—S—R) might be regarded as highly unsymmetrical disulphides or diselenides. Some simple thiolselenenates have now

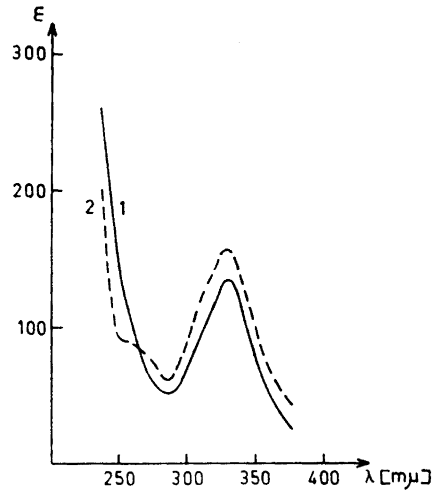


Fig. 8. UV-absorption of: 1. 4,4-Dimethyl-1,2-dithiolane (X). 2. 4,4-Bis-hydroxymethyl-1,2-dithiolane (IX).

been prepared and investigated[21]. The spectrum of ethyl thiolselenenate (XXI) given in Fig. 13 shows only one peak at 285 mμ. This compound is rather unstable and upon heating decomposes into diethyl diselenide and diethyl disulphide which is also given in Fig. 13.

The study of the cyclic 1-thia-2-selena-cyclopentane-4-carboxylic acid (XXII) further confirmed the similarity between the thiolselenenates and the

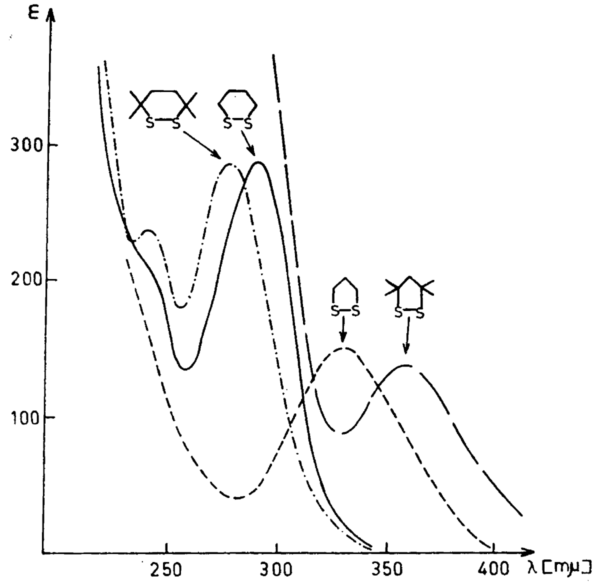


Fig. 9. UV-absorption of the methylsubstituted derivatives VII and VIII as compared with that for the unsubstituted rings.

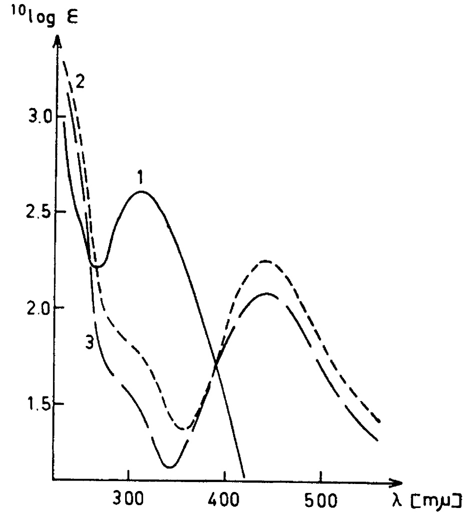


Fig. 10. UV-absorption of: 1. Diethyldiselenide (XI). 2. 4,4-Bis-hydroxymethyl-1,2-diselenolane (XII). 3. 6,8-Selenoctic acid (XIII).

symmetrical disulphides and diselenides[23]. This acid shows a single peak at 386 mμ as shown in Fig. 14 where the spectra of 1,2-dithiolane-4-carboxylic acid and 1,2-diselenolane-4-carboxylic acid (XXIII) and (XXIV) are given for comparison.

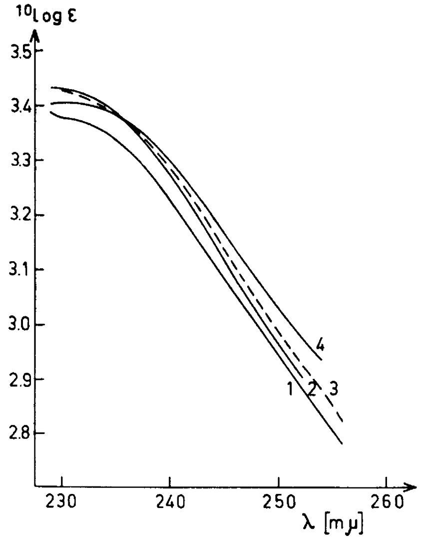


Fig. 11. UV-absorption of: 1. Trichloromethyl-methyldisulphide (XIV). 2. Trichloromethyl-ethyldisulphide (XV). 3. Trichloromethyl-isopropyldisulphide (XVI). 4. Trichloromethyl-*t*-butyldisulphide (XVII).

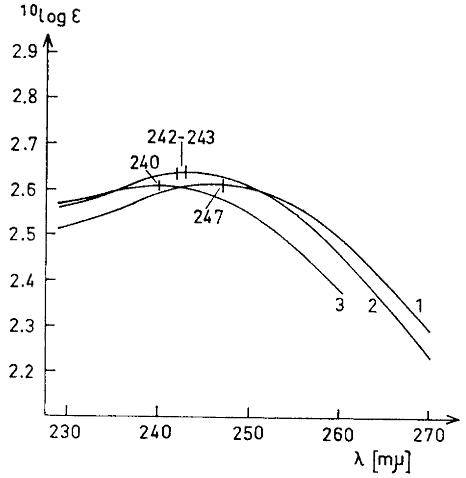


Fig. 12. UV-absorption of: 1. *t*-Butyl-methyldisulphide (XVIII). 2. *t*-Butyl-ethyldisulphide (XIX). 3. *t*-Butyl-isopropyldisulphide (XX).

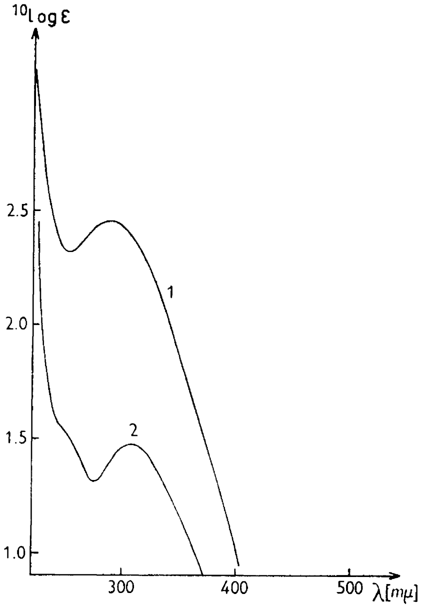


Fig. 13. UV-absorption of: 1. Ethylthiolselenenate (XXI). 2. The decomposition products of (XXI). *i.e.* diethyldisulphide and diethyldiselenide.

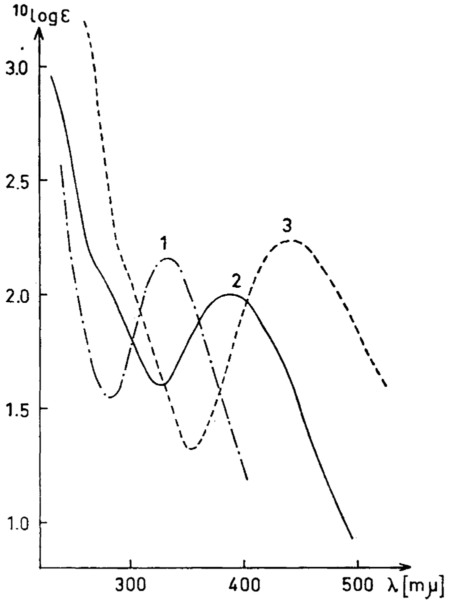


Fig. 14. UV-absorption of: 1. 1,2-Dithiolane-4-carboxylic acid (XXIII). 2. 1-Thia-2-selena-cyclopentane-4-carboxylic acid (XXII). 3. 1,2-Diselenolane-4-carboxylic acid (XXIV).

Accordingly, we conclude that there is no splitting of the first absorption band due to the asymmetry in unsymmetrical disulphides and diselenides or thiolselenates. Reference should also be made to the spectra of some amino-substituted 1,2-dithiolane derivatives which have recently been investigated[34].

$Cl_3C-S-S-CH_3$ XIV

$Cl_3C-S-S-CH_2-CH_3$ XV

$Cl_3C-S-S-CH(CH_3)_2$ XVI

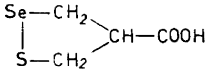
$Cl_3C-S-S-C(CH_3)_3$ XVII

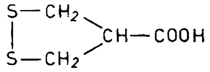
$(CH_3)_3C-S-S-CH_3$ XVIII

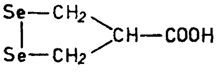
$(CH_3)_3C-S-S-CH_2-CH_3$ XIX

$(CH_3)_3C-S-S-CH(CH_3)_2$ XX

$C_2H_5-Se-S-C_2H_5$ XXI


XXII


XXIII


XXIV

THE SPECTRA OF CARBOXYL- AND CARBONYL-SUBSTITUTED DISULPHIDES

During the last six years much work has been done at the Uppsala school on absorption spectra of carboxyl-substituted disulphides and diselenides. Before discussing these studies, attention must be paid to important early work by Fehnel and Carmack[24] on monosulphides. Among other things they have investigated the UV-spectra of ketosulphides of the type (XXV—XXVII). For the compound (XXVII) where the sulphur atom and the carbonyl group are separated by two saturated carbon atoms, the absorption spectrum is almost exactly a superposition of the spectra for a sulphide and a ketone. In compound (XXV), however, an absorption peak at about 300 mμ ($^{10}\log \varepsilon \approx 2.5$) appears. This peak is also present in the methyl-substituted compound (XXVI).

Fehnel and Carmack also investigated the esters (XXVIII—XXX). When the sulphur atom is separated from the ester group by only one carbon atom as in (XXVIII) a new band at 247 mμ ($^{10}\log \varepsilon \approx 2.57$) appeared. The spectra of the other esters were superpositions of the spectra for the isolated chromophores.

The nature of the 300 mμ peak in β-ketosulphides has recently been studied by Bergson and Delin[25]. The investigation of solvent effects has revealed that the excited state is less polar than the ground state. This, together with sensitivity of the intensity to the molecular environment, suggests that the absorption is due to a perturbed carbonyl-transition ($n \rightarrow \pi^*$). The interpretations given by Fehnel and Carmack[24] in terms of resonance formulae involving hyperconjugation and charge transfer are not in accordance with our experi-

$C_2H_5—S—CH_2—CO—CH_3$ XXV

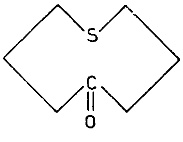
$C_2H_5—S—C(CH_3)_2—CO—CH_3$ XXVI

$C_2H_5—S—CH_2—CH_2—CO—CH_3$ XXVII

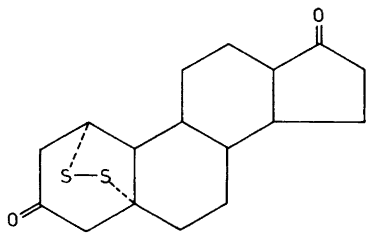
$n—C_4H_9—S—CH_2—COOC_2H_5$ XXVIII

$n—C_4H_9—S—CH_2—CH_2—COOC_2H_5$ XXIX

$S(CH_2—CH_2—COOC_2H_5)_2$ XXX



XXXI



XXXII

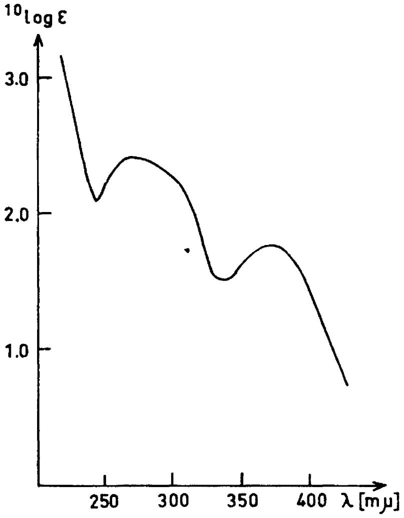


Fig. 15. UV-absorption of: 1α,5α-Epidithio-androstane-3,17-dione (XXXII).

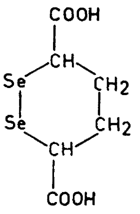
mental findings. We have also investigated some similar selenium derivatives and these too show relatively strong bands in the 300 mμ region [26].

Recently, Leonard *et al.*[27] found a strong interaction between the carbonyl group and the sulphur atom in the cyclic sulphide-ketone (XXXI). This interaction is, however, of a kind different from that discussed above and is best interpreted in terms of charge-transfer.

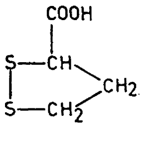
There are evidently two kinds of interaction between a divalent sulphur atom and a carbonyl group. The first causes a perturbation of the $n \rightarrow \pi^*$ transition and the second leads to charge-transfer. In order to distinguish between the two alternatives a careful study of solvent effects is necessary. It appears, however, that the charge-transfer effect is characterized by higher intensity and larger departure from the normal carbonyl-wavelengths than the perturbed transitions. Accordingly the effects to be described below are perhaps best interpreted as perturbed carbonyl- or carboxyl-transitions. For a more detailed discussion of the nature of the carboxyl-transitions we refer to the paper by Bergson and Delin [26].

In view of these considerations the detection of similar phenomena in disulphides is scarcely unexpected. The first observation of such an effect was recently made for 1α,5α-epidithioandrostane-3,17-dione (XXXII) where a pronounced absorption peak at 268 mμ appeared [20,28]. The spectrum of this compound is given in Fig. 15 and should be compared with the curve given for 1α,5α-epidithioandrostane-3α,17β-diol in Fig. 2. It is evident that the simultaneous presence of the disulphide and the carbonyl group is necessary for the appearence of the peak at 268 mμ. A detailed analysis of the 268 mμ band reveals that it is in fact composed of two bands, the one occurring at the longer wavelength having the lower intensity. This band is certainly due to the keto-group in the 17-position, which is not so strongly perturbed as that in the 3-position. An attempt can now be made to understand the spectra of the carboxylic substituted disulphides and diselenides in terms of the

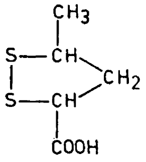
$HOOC-(CH_2)_n-Se-Se-(CH_2)_n-COOH$ XXXIII



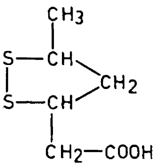
XXXIV



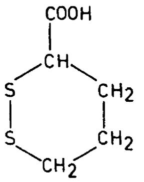
XXXV



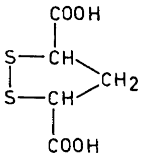
XXXVI



XXXVII



XXXVIII



XXXIX

effects discussed above. The acids with the general formula (XXXIII) are considered first. When n = 4 the compound shows a maximum at 311 mμ and the spectrum is in all respects similar to those of simple unsubstituted diselenides. This is also almost true when n = 3 and n = 2, although in these instances a small hypsochromic shift is observed. The maxima are at 308 and 306 mμ when n = 3 and n = 2, respectively. Diselenium-diacetic acid (n = 1) also has an absorption band in the 300 mμ region, but the maximum cannot be determined with certainty owing to overlap by a stronger band with a maximum at 229 mμ. The hypsochromic shift produced by the α-placed carboxylic group is not great, however, as is clearly seen in Fig. 16. It is therefore impossible to draw definite conclusions about its origin. Nevertheless the peak at 229 mμ is not the peak characteristic of the diselenide group, but it may be a perturbed carboxylic absorption band. In diselenium-α-di-propionic acid and diselenium-α-di-isobutyric acid there is also a strong peak at shorter wavelengths together with the usual diselenide peak in the neighbourhood of 300 mμ [9].

The comparison of the spectra of the carboxylic substituted linear disulphides with the corresponding diselenides shows that the diselenides are more suitable for study for the reasons given in the introduction. A typical disulphide peak at 250 mμ is shown by β,β'-dithio-dipropionic acid and γ,γ'-dithio-dibutyric acid, but dithio-diacetic acid shows only end-absorption [29,30]. Judging by the high intensity of the absorption at 250 mμ (Fig. 17) it is evident that the disappearence of the disulphide band is not a real effect. It is also evident that there is another strong band with a maximum below 250 mμ. The same considerations apply also to dithio-α,α'-dipropionic acid and to dithio-α,α'-diisobutyric acid.

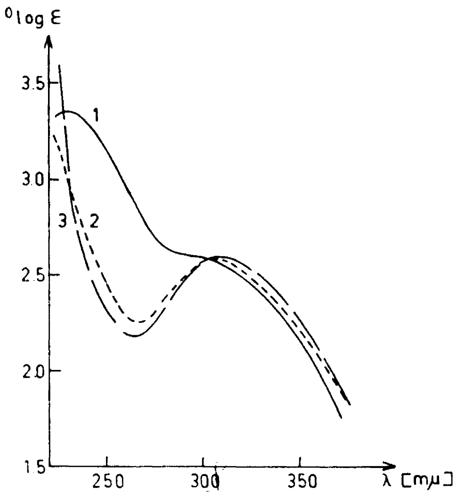


Fig. 16. UV-absorption of the acids (XXXIII). 1. n = 1; 2. n = 2; 3. n = 3.

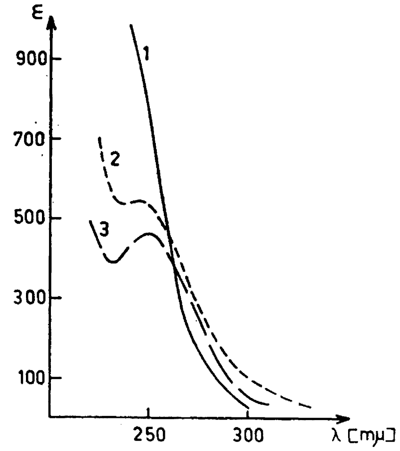


Fig. 17. UV-absorption of:
1. $HOOC-CH_2-S-S-CH_2-COOH$.
2. $HOOC-(CH_2)_2-S-S-(CH_2)_2COOH$.
3. $HOOC-(CH_2)_3-S-S-(CH_2)_3-COOH$.

The six-membered cyclic compound (XXXIV), rac-1,2-diselenane-3,6-dicarboxylic acid, has its first absorption maximum at 343 mμ (Fig. 18). This should be compared with that for the unsubstituted ring at 365 mμ [9]. This difference corresponds to only 0.8 kcal mole^{-1} in excitation energy. In addition it has a band with maximum at about 280 mμ which is strongly

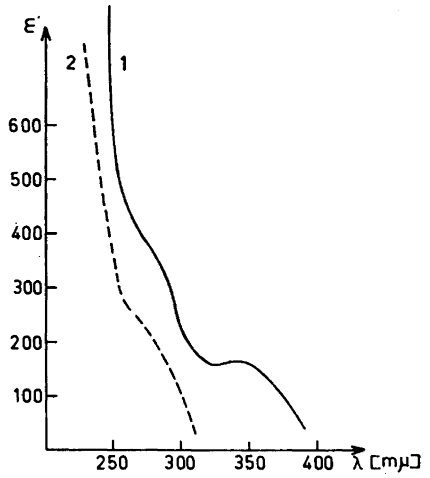


Fig. 18. UV-absorption of: 1. Rac-1,2-diselenane-3,6-dicarboxylic acid (XXXIV). 2. Rac-1,2-dithiane-3,6-dicarboxylic acid.

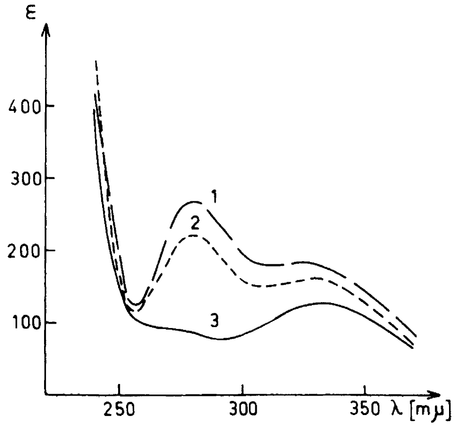


Fig. 19. UV-absorption of 1,2-dithiolane-3-carboxylic acid (XXXV). 1. in 0.6 M HCl. 2. in ethanol. 3. in 0.01 M NaOH.

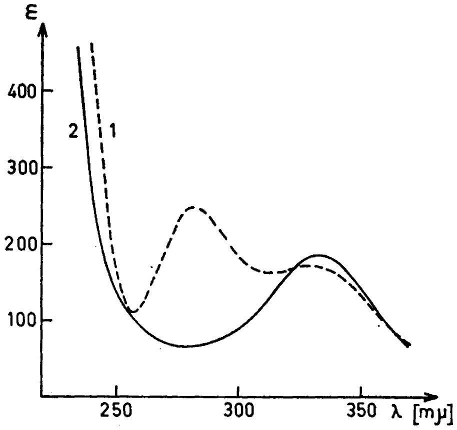


Fig. 20. UV-absorption of: 1. 5-Methyl-1,2-dithiolane-3-carboxylic acid (XXXVI). 2. 5-Methyl-1,2-dithiolane-3-acetic acid (XXXVII).

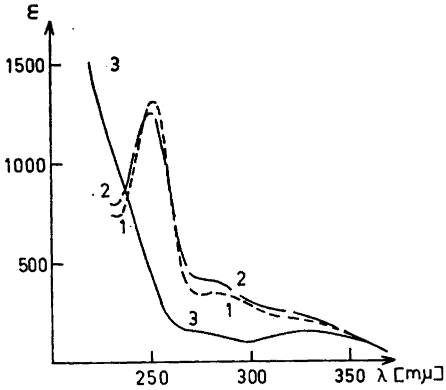


Fig. 21. UV-absorption of: 1. Rac-1,2-dithiolane-3,5-dicarboxylic acid (XXXIX) in 0.1 M H_2SO_4. 2. Rac-dimethyl-1,2-dithiolane-3,5-dicarboxylate (in ethanol). 3. Di-Na-salt of Rac-1,2-dithiolane-3,5-dicarboxylic acid (in water).

overlapped by a band with higher intensity occurring at a shorter wavelength. The 280 mμ band might originate in a transition from the π_{-1} orbital (*cf.* Fig. 7), but this assignment is uncertain. Rac-1,2-dithiane-3,6-dicarboxylic acid has its first absorption band at 275 mμ although it is overlapped by stronger absorptions at shorter wavelengths [30]. The 275 mμ band is displaced little from its position as given by the unsubstituted ring (290 mμ). A possible $\pi_+ \rightarrow \sigma_-$ transition cannot be detected with certainty in this instance owing to the strong absorption at shorter wavelengths, but it can be seen in the unsubstituted 1,2-dithiane and in 3,3,6,6-tetramethyl-1,2-dithiane (Fig. 9).

Among the five-membered acids Claeson [31] has studied 1,2-dithiolane-3-carboxylic acid (XXXV) and 5-methyl-1,2-dithiolane-3-carboxylic acid (XXXVI). Both acids show the typical absorption peak occurring at about 330 mμ and in addition a strong band at 280 mμ is present. This band does not occur when there is a $-CH_2-$ group between the ring and the carboxylic group as was found in (XXXVIII) (Fig. 20), and of course not when the group is as remote as it is in 6,8-thioctic acid. [*Cf.* also 1,2-dithiolane-3-carboxylic acid with 1,2-dithiolane-4-carboxylic acid (Fig. 14) and 1,2-dithiane-3-carboxylic acid with 1,2-dithiane-4-carboxylic acid [32]. We conclude that the 280 mμ band is best interpreted as a perturbed carboxylic transition, an assignment which is substantiated by its disappearance in alkaline solution (Fig. 19). Similar decreases in the intensity of the bands at short wavelengths as a result of salt formation has also been observed by Schotte for dithio-diacetic acid and 1,2-dithiane-3,6-dicarboxylic acid [30], and by Claeson [33] for 2-methyl-3,4-dithiahexanoic acid.

The existence of a short-wavelengths absorption band which disappears on salt formation is also found in 1,2-dithiane-3-carboxylic acid [31] (XXXVIII), 1,2-dithiane-3,6-dicarboxylic acid and in the five-membered 1,2-dithiolane-

3,5-dicarboxylic acid (XXXIX), which has been carefully investigated by Schotte[29,30]. The methyl ester of this acid has a spectrum very similar to that of the free acid (Fig. 21). The free acid, the ester, and also the salt have the typical 1,2-dithiolane peak in the neighbourhood of 330 mμ. The strong absorption band with maximum at 250 mμ is certainly a perturbed carboxylic transition. In addition to the peaks just mentioned there is also one with maximum at about 280 mμ. This might be another perturbed carboxylic transition.

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