

Electronic Absorption Spectra of Unconjugated Alkyl Thials and Thiones

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The electronic spectra of a number of simple aliphatic thials and thiones have been evaluated. The C=S compounds were obtained together with the corresponding thiols by photolysis of disulfides in hydrocarbon glasses at 77°K. Besides the previously known absorption in the visible region ($n \rightarrow \pi^*$ transition), two peaks were recorded in the far ultraviolet, one of which was seen only at room temperature. By comparison with analogous oxygen compounds the two peaks were attributed to $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, the latter, disappearing at 77°K, occurring from a vibrationally excited level.

When the solutions were stored at room temperature the intensity of the thiocarbonyl absorption gradually disappeared. For one compound, ethanethial, the disappearance was shown to correspond to a simultaneous formation of the trimer, 2,4,6-trimethyl trithiane.

Much work has been devoted to the study of the spectral behaviour of simple alkyl compounds containing a chromophor with a multiply bonded basic group such as $>C=O$, $-NO_2$, $-N=O$, $-N=N-$. The thiocarbonyl group belongs to this category; however, very little is known about the light absorption of pure aliphatic thials or thiones without a second heteroatom. Some alicyclic thiones, including cyclopentane- and cyclohexane-thione, have been reported by Sen¹ to show a red color when freshly distilled. In a second paper² the author gives more precise data for the light absorption of benzene solutions of thiocamphor, thiofenchone and bithiocamphor, all of which show an absorption band between 527 and 453 $m\mu$ with a peak at 495 $m\mu$. Janssen³ has recorded the spectrum of cyclohexanethione and reports λ_{max} at 495 and 504 $m\mu$ in ethanol and cyclohexane, respectively: ϵ_{max} lies between 1 and 10.

Our lack of knowledge concerning the simple aliphatic thiocarbonyl compounds can be ascribed to their instability. According to the literature most attempts to synthesize them yield the trimer or some other polymer as a pro-

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duct. Comprehensive reviews summarizing the various methods of preparation have been published by Campaigne ⁴ and by Reid ⁵.

It has previously been reported that in photolysis experiments ⁶ with dialkyl disulfides aiming at the production and trapping of thiyl radicals at liquid nitrogen temperature, the instantaneous stoichiometrically simple over-all reaction was found to be:



R = H or Alk.

The absence of disturbing side reactions together with the fact that the amount of conversion could easily be determined allowed an evaluation of the UV-spectrum of the thiocarbonyl compounds formed *. The analogous disproportionation reaction has been reported to occur when alicyclic disulfides are pyrolysed; for instance, bornyldisulfide is reported to yield thiocamphor and thioborneol (Ref.⁴, pp. 32, 33).

EXPERIMENTAL TECHNIQUE AND MATERIALS

The spectra were taken using a Unicam Model SP 700 recording double-beam spectrophotometer. A specially designed unit allowing two identical quartz cells (diam. 19 mm, path length 17 mm) to be kept at liquid-nitrogen temperature was substituted for the standard cell-compartment. The wavenumber scale was calibrated using spectral lamps (Zn and Hg, low pressure) and the error in transmission values introduced by stray-light was found to be negligible in any case up to 50 kc.cm^{-1} .

The photolysis set-up consisted of two super high-pressure mercury lamps (900 W each), together with appropriate cooling and filter devices. The disulfides were irradiated in hydrocarbon mixtures that formed fully transparent glasses at 77°K. Most experiments were performed with isopentane/3-methyl pentane (6:1).

Further details are given elsewhere concerning the low-temperature cell compartment ⁷, the general experimental procedure ⁸ as well as the methods for preparation and purification of the disulfides ⁸ and the purification of the hydrocarbons ⁹.

RESULTS

The disulfides were all photolysed in 0.05 and 0.4 mM solutions. For the lowest concentration the most striking spectral change, besides the disappearance of the disulfide peak, was the appearance of a strong absorption peak at about 45 kc.cm^{-1} (stable at 77°K). The rate of increase in intensity of this peak corresponds to its formation from a first-order decay of the disulfide. This fact allowed an evaluation of the shape of the peak after all of the disulfide had been photolyzed. From the kinetic plot the fraction of the disulfide that had been decomposed at the end of photolysis could be determined; this fraction was always kept at 70–90 %. The extrapolated peak was attributed to the presence of both the thiocarbonyl compound and the mercaptan. By subtracting the calculated absorbance of the known amount of mercaptan the UV-absorption of the thiocarbonyl compound at 77°K was obtained.

The experimental conditions allowed a spectrum to be recorded 4–5 min after the irradiated cell had been brought to room temperature. From this

* However, during photolysis of 0.25 mM dimethyl disulfide a side-reaction was found to occur to some extent (*cf.* Ref.⁶).

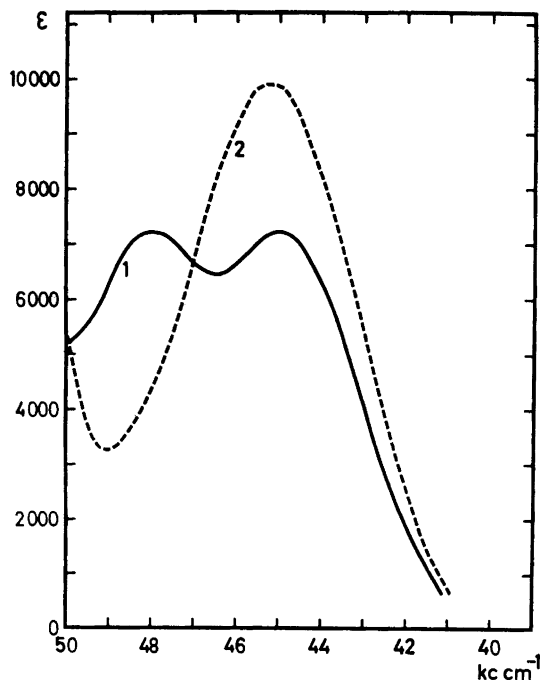


Fig. 1. Ultraviolet spectrum of butanethial at room temperature (1) and at 77°K (2).

measurement the spectrum of the thiocarbonyl compound could be evaluated by subtracting the absorbance of the mercaptan and the remaining disulfide. Figs. 1–3 show the evaluated spectra obtained in typical runs with three disulfides. The spectral characteristics at 77 and 298°K are summarized in Table 1 for all disulfides investigated. When the irradiated solutions were stored at room temperature the transmission at the thiocarbonyl peak slowly increased. (*cf.* Fig. 9 in Ref.⁶) However, when a 0.4 mM disulfide solution was photolyzed the rate of the spectral change of the thiocarbonyl compounds, after warm-up, was much faster. Fig. 4 gives the spectra recorded at various times for an ethanethial solution, showing a well-defined isosbestic point at 40.4 kc.cm⁻¹. The decrease in absorption is caused by the formation of the trimer, which is a 1,3,5-trithiacyclohexane derivate. This is illustrated in Fig. 5, which gives the absorption spectra of ethanethial and one third of that of its trimer, corresponding to the conversion of 1 mole of monomer to 1/3 mole of trimer.

A photolysis experiment with diethyl disulfide was also carried out at 2 mM concentration. The rate of photolysis could be followed by observing the decrease in the disulfide absorption at 35–36 kc.cm⁻¹. After 80 min of irradiation 74 % of the disulfide had been converted to mercaptan and thial. The sample now had a pale red color and after warm-up a very weak absorption

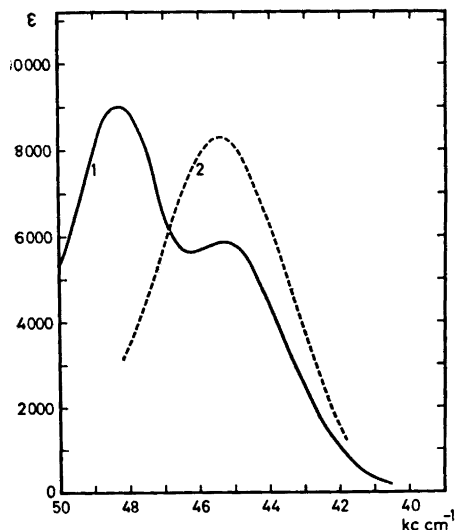


Fig. 2. Ultraviolet spectrum of ethanethial at room temperature (1) and at 77°K (2).

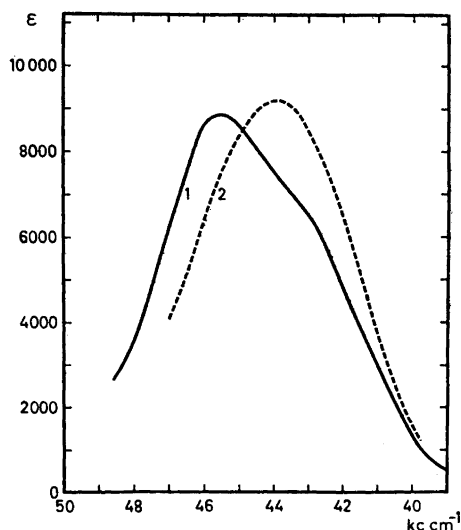


Fig. 3. Ultraviolet spectrum of 2-propanethione at room temperature (1) and at 77°K (2).

Table 1. Ultraviolet spectrophotometric characteristics at 77 and 298°K for various alkyl thiocarbonyl compounds. Figures in parentheses indicate the number of experiments. The uncertainties are expressed as mean deviations.

	At 77°K		At 298°K	
	Wavenumber of peak kc.cm ⁻¹	log ε _{max}	Wavenumber of peak(s) ^a kc.cm ⁻¹	log ε _{max}
Methanethial	48.07 (1)	(3.8)	b)	b)
Ethanethial	45.50 ± 0.05 (5)	3.90 ± 0.03 (3)	48.2 (3)	3.89 ± 0.07 (3)
Propanethial	45.27 ± 0.05 (2)	4.0 ± 0.1 (1)	45.3 (3)	3.72 ± 0.07 (3)
Butanethial	45.21 ± 0.03 (7)	3.93 ± 0.03 (6)	48.0 (2)	3.90 ± 0.09 (2)
2-Methylpropanethial	45.06 ± 0.02 (2)	3.90 ± 0.07 (2)	45.3 (2)	3.79 ± 0.06 (2)
2,2-Dimethylpropanethial	44.97 ± 0.02 (2)	4	47.9 (4)	3.85 ± 0.02 (4)
2-Propanethione	44.00 ± 0.03 (2)	3.95 ± 0.02 (2)	45.0 (5)	3.83 ± 0.05 (5)
2-Butanethione	44.03 ± 0.04 (3)	3.93 ± 0.02 (2)	47.9 (2)	3.77 ± 0.04 (2)
Cyclohexanethione	44.60 ± 0.03 (2)	3.90 ± 0.04 (2)	45.2 (2)	3.80 ± 0.05 (2)
			47.7 (2)	3.90 ± 0.03 (2)
			45.0 (2)	3.85 ± 0.02 (2)
			45.5 (2)	3.96 ± 0.02 (2)
			S 43 (2) ^c	3.83 ± 0.02 (2)
			45.4 (2)	3.87 ± 0.02 (2)
			S 43.5 (2)	3.83 ± 0.02 (2)
			44.8 (2)	3.76 ± 0.02 (2)

^a The uncertainty of all values in this column is ± 0.1 kc.cm⁻¹.

^b At room temperature the methanethial solution only shows a steadily increasing absorption towards the vacuum ultraviolet.

^c S = shoulder.

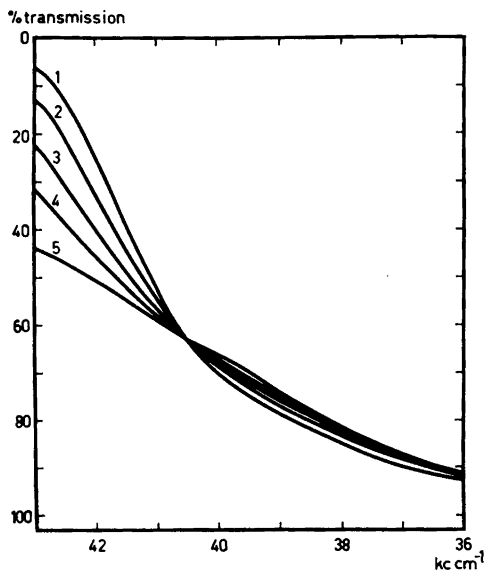


Fig. 4. Ultraviolet spectra of 0.4 mM ethanethial 5 min (1), 15 min (2), 30 min (3), 1 h (4) and 3.5 h (5) after warm-up.

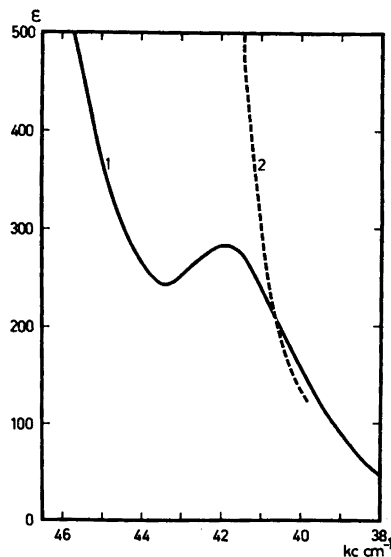


Fig. 5. Ultraviolet spectra of 2,4,6-trimethyl trithiane (1) and ethanethial (2). One third of the molar extinction for the trimer has been plotted.

peak was recorded between 17–23 kc.cm^{-1} ; the transmission at the maximum at 19 kc.cm^{-1} was reduced by 4%. These observations gave a calculated ϵ_{max} of 6 ± 2 for the thiocarbonyl absorption in the visible. When photolyzed in 5 mM solutions ethyl, butyl and cyclohexyl disulfide all showed a red color and an absorption band between 17 and 24 kc.cm^{-1} , with a peak at about 19–20 kc.cm^{-1} . At this concentration the mercaptan formed during the primary photolysis process is photolyzed to a significant extent and the high UV-absorption of the secondary photolysis products¹⁰ interferes with the disulfide and thiocarbonyl absorption, preventing an evaluation of ϵ_{max} for the thiocarbonyl band.

The spectrum of cyclohexanethione has been reported by Janssen³ to have no strong absorption band ($\log \epsilon > 3.5$) at wavenumbers below 45.5 kc.cm^{-1} . As previously reported⁶ a dilute solution of freshly distilled cyclohexanethione showed a broad band around 45 kc.cm^{-1} both at 77 and 298°K.

DISCUSSION

A. Classification of bands

With respect to their intensity, wavenumber region and different behaviour at 77°K and room temperature the absorption bands of the thiocarbonyl compounds can be divided into three types:

1. An absorption in the visible region of low molar extinction. For ethanethiol, butanethiol and cyclohexanethione the absorption band ranged from 17 to 23 kc.cm^{-1} with a peak at 19–20 kc.cm^{-1} . This band will be classed as a Type I band.

2. At 77°K all compounds listed in Table I showed a characteristic absorption band in the far ultraviolet. The peak wavenumber of this band, which will be classified as a Type II band, seemed to be slightly dependent on the molecular structure. At 77°K it was found between 45.5 and 45.2 kc.cm^{-1} for the straight-chain alkane thiols investigated, for branched chain thiols the absorption was slightly displaced towards lower wavenumbers. The thione peak was found at 44.0 kc.cm^{-1} for alkane thiones and at 44.6 kc.cm^{-1} for cyclohexanethione. The molar extinction at 77°K was about the same for both thiones and thiols ($\log \epsilon_{\text{max}}$ 3.9–4.0).

The position of the absorption peaks changed only slightly when the solutions were brought to room temperature. However for thiones, the Type II peak became distinguishable only as shoulder, owing to the appearance of a second band (see below). For menthanethiol the peak was not discernable at all at room temperature; the spectrum only showed a monotonously increasing absorption towards the vacuum-ultraviolet. This absorption, however, decreased at a normal rate when the methanethiol was left at room temperature for a longer period of time (see above).

3. When the irradiated solution was brought to room temperature, a second band (Type III) was found in the far ultraviolet for all thiocarbonyl compounds investigated except methanethiol and cyclohexanethione. The position of the peak, at 47.9–48.0 kc.cm^{-1} for straight-chained thiols and at 45.5 kc.cm^{-1} for thiones, indicates a stronger influence of molecular structure upon the peak position than was found for the Type II band. The Type III band invariably disappeared upon cooling to 77°K and reappeared upon warm-up*.

B. Preliminary assignment of the bands

A low-intensity band has been reported for a number of thiones, mainly conjugated with a second heteroatom like N, S, or O. It was early postulated¹¹ that this absorption is due to a $n \rightarrow \pi^*$ transition according to the terminology suggested by Kasha¹². Janssen¹³ has shown a rectilinear relation between the transition energies calculated by a LCAO–MO treatment of the various thio-ketones and the peak wavenumber of the Type I band. His investigation included the unconjugated thiocarbonyl group for which the calculated energy value for the $n \rightarrow \pi^*$ transition corresponds to an absorption maximum at

* The possibility that the protomeric enethiol-form is responsible for the Type III peak and that the disappearance of this peak upon cooling to 77°K corresponds to a change in equilibrium towards the thiol- or thione-forms can be ruled out for the following reasons. In the first place, the protomerization should be too slow in the non-polar solvent to allow the required very rapid conversion when the solution is brought from room temperature down to 77°K within 5 min. Secondly, this suggestion seems to be excluded owing to the fact that 2,2-dimethylpropanethiol (from neopentyl disulfide) did show a normal behaviour — that is, the Type III peak existed at room temperature and vanished upon cooling. This compound does not have an α -hydrogen atom and therefore cannot exist in the enethiol-form.

20 kc.cm^{-1} . This is in good agreement with the value reported for cyclohexanethione³ and the values for ethanethial, butanethial and cyclohexanethione from this investigation.

Although a definite assignment of the Type II and III bands is not possible with the experimental evidence available, their molar extinction values strongly indicate that they are connected with symmetry-allowed transitions. Some preliminary information about their origin can be gained from a comparison between the thiocarbonyl compounds and their oxygen analogues, aldehydes and ketones. For formaldehyde, acetaldehyde and acetone two absorption bands have been reported in the vacuum ultraviolet, one around 55 and the other around 60 kc.cm^{-1} ; Ref.¹⁴, p. 306. The transitions involved are $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, respectively, both being allowed by local symmetry in the CO and CS groups¹⁵. From experimental evidence, summarized in the following three points, it can be shown that it is plausible to find these two transitions displaced towards lower wavenumbers in alkylthiocarbonyl compounds:

1. In thiocarbonates and thiocarboxyl acid derivatives the $\pi \rightarrow \pi^*$ band is found at lower wavenumbers than in the carbonates and carboxylic esters. This indicates a smaller energy separation for the π - and the π^* -orbitals in the thiocarbonyl than in the carbonyl group; Ref.¹⁴, p. 314.

2. Measurements of the ionization potential results in a lower value for the sulfur lone-pair electrons than for the corresponding oxygen electrons¹⁶. Thus in the thiocarbonyl group the n -level is of higher energy than in the carbonyl group.

3. The C—S bond dissociation energy is lower than that of the C—O bond¹⁷ and it is plausible to assume the same statement to be true for the σ^* antibonding states.

Janssen has shown that a linear relationship exists between calculated transition energy values and the wavenumbers for the $\pi \rightarrow \pi^*$ bands for conjugated molecules of the type A.CS.B¹³. He has also calculated the transition energy value for the unconjugated C=S group to 1.812 β . This should correspond to an absorption of about 46 kc.cm^{-1} as judged from a rather remote extrapolation of the straight line given by Janssen.

In a study of the relation between spectra and electronic orbitals, Walsh¹⁸ has pointed out that for molecules of the type H_2AB the binding energy of the upper repulsive state of that orbital which is formed from $2p_{x(A)}$ and $2p_{x(B)}$ increases with increasing non-planarity of the molecule. Formaldehyde and — by analogy — thioformaldehyde have planar ground states with no electron in the orbital referred to (a π^* -orbital in the planar configuration); instead all occupied orbitals are at the lowest energy levels in the planar state. If, however, an electron is promoted from one of these orbitals to an orbital striving towards non-planarity of the molecule the result may be a structure which is pyramidal at equilibrium in the excited state. An example of this is the $n \rightarrow \pi^*$ transition, where in fact for formaldehyde in the upper state an angle greater than 25° is found between the plane of the methylene group and the carbonyl axis¹⁹ and progressions of the out-of-plane bending vibrations (ν_6) appear in the fluorescence spectrum. Besides this angle deformation, formaldehyde also shows a considerably increased carbonyl bond length in the excited state, 1.32 Å as compared with 1.22 in the ground state.

Compared with the situation for the $n \rightarrow \pi^*$ transition an even greater out-of-plane angle can be expected for the state reached by a $\pi \rightarrow \pi^*$ transition, as in this case the promoted electron is taken from an orbital where its presence contributes more to stabilize the planar structure than a non-bonding electron does. The transformation of a bonding electron to a non-bonding electron would also cause a further increase of the A—B bond length than that found for the $n \rightarrow \pi^*$ transition. Considering these large structural changes of the molecule accompanying a $\pi \rightarrow \pi^*$ transition, the energy required must be considerably lower if the transition takes place from a vibrationally excited state than from the ground state, provided the excited vibration includes the molecular changes involved. A non-planar structure for the excited state involving a π^* -orbital can also be expected for compounds where alkyl groups have been substituted for one or both hydrogen atoms -- that is, for aldehydes, ketones, thials and thiones.

In contrast to the π -orbital the antibonding state of the carbonyl σ -orbital has a lowest energy level corresponding to a planar structure¹⁸. However, an increased carbonyl bond length is expected also in this case.

Taking the above arguments into consideration it seems reasonable to make the following assignments:

Type II: a $n \rightarrow \sigma^*$ band, corresponding to transitions from the vibrational ground state.

Type III: a $\pi \rightarrow \pi^*$ band corresponding to transitions from a vibrationally excited level. At 77°K the population of this level is decreased and the band disappears.

The intensity of the Type III band corresponds to a population of the excited vibrational state of not less than 10 % at room temperature and a ratio between the population at room temperature and that at 77°K of at least 10. These two requirements fix the wavenumber of the vibration involved to lie between 165 and 480 cm^{-1} . These figures sound reasonable for an out-of-plane bending vibration of the molecule. If the force constant for this vibration is put equal to 1/2 the value reported for formaldehyde²⁰ (a relationship applicable to phosgen thiophosgen^{20,21}) an estimated wavenumber of 770 cm^{-1} is found for methanethial and 290 cm^{-1} for propanethione. The high value calculated for methanethial corresponds to only 2.5 % of the molecules in the first excited level at room temperature and is in agreement with the fact that a significant Type III band is absent in the thioformaldehyd spectrum. For cyclohexanethione the ring structure is expected to render the out-of-plane bending vibration more difficult, which may be the reason why the Type III band is not found in this compound.*

The assignment of the Type III band to a $\pi \rightarrow \pi^*$ transition also agrees with the expected influence from molecular structure¹⁵. On the contrary the $n \rightarrow \sigma^*$ transition is less sensitive to conjugation and ought to be found in the same wavenumber region also for simple conjugated molecules. In fact, Sandström

* *Added in proof:* Dr. B. Bak, Copenhagen, has pointed out that ring vibrations $< 480 \text{ cm}^{-1}$ should be present in cyclohexanethione, facilitating the discussed out-of-plane bending vibration. However, the band may be too weak to be observed.

recently reported²² a band at 43 kc.cm^{-1} for thioacetamide in addition to the already known $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands^{23,24}. This band may well be the $n \rightarrow \sigma^*$ band since it shows the expected solvent dependence.

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