

The Electronic Spectra of some Derivatives of Xanthic, Dithiocarbamic and Trithiocarbonic Acids

M. L. SHANKARANARAYANA

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen,
The H. C. Ørsted Institute, Copenhagen, Denmark*

and C. C. PATEL

*Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 12, India*

The electronic spectra of some derivatives of xanthic, dithiocarbamic and trithiocarbonic acids have been studied in different solvents. Based on solvent effect and other considerations, the low intensity long wavelength band is assigned to $n \rightarrow \pi^*$ while the intense bands at low wavelength region to $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions.

Recently Janssen *et al.*,¹ Rao and coworkers,^{2,3} Rosengren,⁴ Sandström,⁵ and Fabian and Mayer⁶ studied the electronic spectra of a number of thiocarbonyl compounds and assigned the various bands to electronic transitions based on solvent effect, etc. In this paper, the spectra of some of the derivatives of xanthic ($\text{RO}-\text{C}(=\text{S})-\text{SH}$), dithiocarbamic ($\text{R}_2\text{N}-\text{C}(=\text{S})-\text{SH}$) and trithiocarbonic ($\text{RS}-\text{C}(=\text{S})-\text{SH}$) acids are reported and their absorption peaks are characterised to be due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions.

EXPERIMENTAL

Compounds. Potassium alkyl xanthates,⁷ dimethyl dixanthogen,⁸ dibutyl xanthogen monosulphide,⁹ *S*-carboxymethyl-*O*-butyl xanthate,¹⁰ diethylammonium *N,N*-diethyl-dithiocarbamate, piperidinium pentamethylene dithiocarbamate¹¹ and *S,S*-dibutyl dithiobis(dithioformate)¹² were prepared, purified and analysed by standard methods. Sodium di-isopropyl dithiocarbamate was kindly supplied by Dr. C. W. Pluygers (Organic Chemistry Institute, T.N.O., Utrecht, Netherlands) and tetramethyl, tetraethyl, tetra-butyl and dicyclopentamethylene thiuram disulphides by Robinson Brothers, Ltd., (West Bromwich, England), tetra-isopropyl thiuram disulphide¹³ was prepared by oxidation of sodium di-isopropyl dithiocarbamate with iodine. Potassium butyl trithio-

Table 1. Peak wavelengths and molar extinction coefficients for some derivatives of xanthic acid.

Compound	Heptane		Ethanol		Acetonitrile		Water	
	λ_{\max} m μ	$\log \epsilon$	λ_{\max} m μ	$\log \epsilon$	λ_{\max} m μ	$\log \epsilon$	λ_{\max} m μ	$\log \epsilon$
Dimethyl dixanthogen	240	4.31	239	4.34	239	4.31		
	278	3.90	279	3.91	282	3.92		
	361	1.94	368	1.94	358	1.92		
Dibutyl dixanthogen ¹⁵	244	4.38	243	4.37	243	4.38		
	286	3.92	287	3.91	288	3.90		
	365	1.91	362	1.92	360	1.92		
Dibutyl xanthogen monosulphide	225	4.30	224	4.34				
	285	3.90	286	3.80				
	365	1.90	363	1.91				
<i>S</i> -carboxy methyl <i>O</i> -butyl xanthate			223	3.90			221	3.92
			280	4.21			281	4.20
			354	1.75			343	1.80
Potassium methyl xanthate			228	3.97			226	3.90
			304	4.31			302	4.28
			382.5*	1.71			381.5*	1.71
Potassium butyl xanthate			229	4.00			229	3.90
			304	4.30			301	1.82
			386	1.80			381	1.82
Potassium iso- pentyl xanthate			229	3.98			229	3.96
			304	4.25			303	4.30
			387	1.75			384	1.72

* Ref. 1

carbonate was supplied by Distillation Products, Rochester (U.S.A.). The substance was recrystallised from alcohol before use.

Solvents. Heptane: Merck reagent was distilled and used. Acetonitrile and ethanol were purified by standard methods.¹⁴

Spectra. The electronic spectra in the near ultraviolet and visible regions were studied with a Hilger spectrophotometer model H-700, using 1 cm quartz matched cells.

RESULTS

The absorption maxima and the intensities ($\log \epsilon$) of the various compounds are given in Tables 1–3. Typical absorption spectral curves of the derivatives of xanthic, dithiocarbamic, and trithiocarbamic acids are given in Figs. 1–6.

DISCUSSION

Weak intensity bands at longer wavelength. The bands exhibited by the derivatives of xanthic, dithiocarbamic, and trithiocarbamic acids (Tables 1–3

Table 2. Peak wavelengths and molar extinction coefficients for some derivatives of dithiocarbamic acid (s = shoulder).

Compound	Heptane		Ethanol		Water	
	λ_{\max} m μ	log ϵ	λ_{\max} m μ	log ϵ	λ_{\max} m μ	log ϵ
Tetramethyl thiuram disulphide	223	4.17	222	4.15		
	250s	—	250s	—		
	278s	3.93	275s	3.96		
	—	—	—	—		
Tetraethyl thiuram disulphide	225	4.20	220	4.10		
	250	4.16	252	3.91		
	278	4.03	276	3.87		
Tetraisopropyl thiuram disulphide	221	4.25	220	4.23		
	254	4.23	259	4.21		
	279	4.21	272	4.21		
	—	—	—	—		
Tetrabutyl thiuram disulphide	220	4.35	218	4.37		
	255	4.19	264	4.20		
	278	4.20	272	4.21		
Dicyclopentamethylene thiuram disulphide	221	4.20	221	4.30		
	252	4.01	254	4.20		
	282	4.01	280	4.19		
	—	—	—	—		
Sodium di-isopropyl dithiocarbamate			—	—	—	—
			258	4.10	257	4.12
			292	4.21	283	4.21
Diethylammonium <i>N,N</i> -di- ethylthiocarbamate			—	—	—	—
			255	4.10	257	4.02
			288	4.00	281	4.01
Piperidinium pentamethylene dithiocarbamate			—	—	—	—
			252	4.15	260	4.11
			284	4.02	280	4.10
		365	1.82	351	1.85	

and Figs. 1—6) show that these compounds exhibit a low intensity absorption band ($\log \epsilon \approx 2$) at longer wavelengths around 360, 350, and 450 m μ , respectively. This band is very sensitive to the solvent used and shows large blue shifts progressively as the solvent is changed from non-polar to polar. The increased blue shift with the increase in the polarity of the solvent shows that the transition energy involved increases with the increase in the polarity

Table 3. Peak wavelengths and molar extinction coefficients for some derivatives of trithiocarbonic acid.

Compound	Heptane		Ethanol		Acetonitrile		Water	
	λ_{\max} $m\mu$	$\log \epsilon$	λ_{\max} $m\mu$	$\log \epsilon$	λ_{\max} $m\mu$	$\log \epsilon$	λ_{\max} $m\mu$	$\log \epsilon$
<i>S,S</i> -Dibutyl dithiobis(dithioformate)	258	3.70	255	3.70	256	3.68		
	306	3.82	308	3.65	310	3.71		
	—	—	—	—	—	—		
Potassium butyl trithiocarbonate	450	1.70	444	1.80	445	1.71		
			235	3.60	236	3.60	235	3.60
			308	3.85	302	3.89	310	3.82
			330–350	3.92	330–350	3.95	330–350	3.94
			430	1.80	446	1.60	425	1.80

of the solvent, due to solvation and/or hydrogen bonding between the non-bonding electrons of the thiocarbonyl group of the solute and the solvent molecules. The low intensity band can be ascribed to the excitation of a non-bonding electron localized on the sulphur atom of a thiocarbonyl group to an antibonding π orbital. This transition is designated as $n \rightarrow \pi^*$ transition in accordance with the empirical rule suggested by Kasha¹⁶ and Sidman.¹⁷ This type of transition has been extensively investigated in thion compounds by Janssen.^{18–20}

It is observed that the $n \rightarrow \pi^*$ band shifts progressively to shorter wavelengths in the following order: trithiocarbonate (450 $m\mu$) > xanthate (360 $m\mu$) > dithiocarbamate (350 $m\mu$). Such a hypsochromic shift is due to the substituents attached to the thiocarbonyl group, $-X-(S-)C=S$, where $X = S, O,$ or N . The lowering of the $n \rightarrow \pi^*$ transition corresponds to the mesomeric electron releasing order $S < O < N$. A similar shift has been observed in compounds containing a carbonyl group by Nagakura²¹ and a thiocarbonyl group by Janssen.²⁰ They interpreted the shifts using the LCAO-MO approximation and found that the blue shifts are due to the raising of the energy of the excited state in relation to that of the ground state. The increase in energy

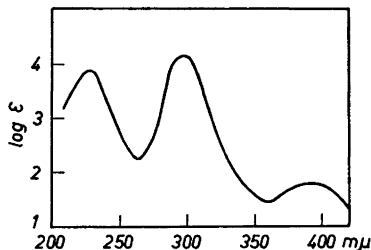


Fig. 1. Spectrum of potassium butyl xanthate in ethanol.

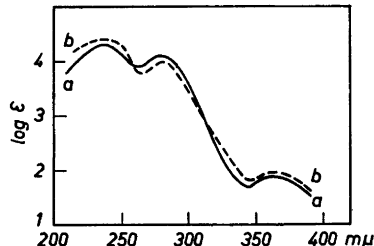


Fig. 2. Spectra of dibutyl dixanthogen (a) in heptane —, (b) in ethanol — —.

is caused by the electron donating substituents attached to the thiocarbonyl group.

The low intensity wavelength band could not be located in the thiuram disulphides probably due to its masking by the intense 280 $m\mu$ band.

Intense bands in the low wavelength region. The intense band ($\log \epsilon \approx 4$) around 260 $m\mu$ in dithiocarbamic acid, 280 $m\mu$ in xanthic, and 310 $m\mu$ in trithiocarbonic acids derivatives shows red shifts on changing from non-polar to polar solvents. This band is ascribed to $\pi \rightarrow \pi^*$ transition and the assignment is in agreement with that given by Kasha¹⁶ and Sidman.¹⁷ It is interesting to

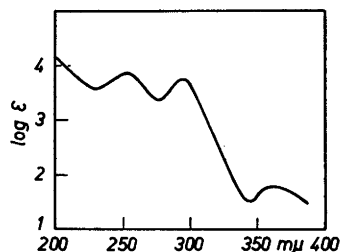


Fig. 3. Spectrum of sodium di-isopropyl dithiocarbamate in ethanol.

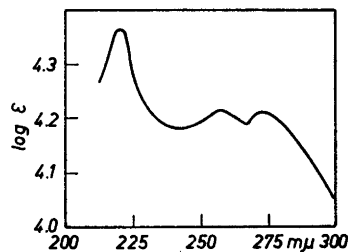


Fig. 4. Spectrum of tetrabutyl thiuram disulphide in ethanol.

note that the $\pi \rightarrow \pi^*$ band immediately precedes the $n \rightarrow \pi^*$ band in the derivatives of xanthic acid and esters of trithiocarbonic acid. But in the derivatives of dithiocarbamic acid and potassium n-alkyl trithiocarbonates, the $\pi \rightarrow \pi^*$ band is followed by two bands — a strong band at 280 $m\mu$ in dithiocarbamate and 330–350 $m\mu$ in trithiocarbonate and a weak band ($n \rightarrow \pi^*$) around 350 and 450 $m\mu$, respectively. Like the $n \rightarrow \pi^*$ band the $\pi \rightarrow \pi^*$ band also shifts to shorter wavelengths with the increase in the electron releasing tendency of the substituent atoms attached to the C=S group.

The intense band around 280 $m\mu$ ($\log \epsilon \approx 4$) in the derivatives of dithiocarbamic acid shows blue shifts with the increase in the polarity of the solvent. Janssen²⁰ ascribed such a band in similar compounds to $n \rightarrow \sigma^*$ transition although the theoretical considerations showed it to be due to $\pi \rightarrow \pi^*$ transition. Rao *et al.*² consider this band to be due to $\pi \rightarrow \pi^*$ transition. To support any

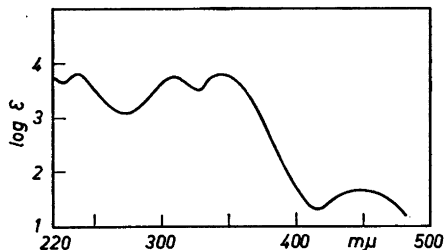


Fig. 5. Spectrum of potassium butyl trithiocarbonate in acetonitrile.

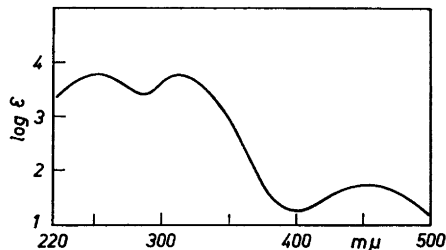


Fig. 6. Spectrum of *S,S*-dibutyl dithiobis(dithioformate) in acetonitrile.

one of the assignments one would expect a similar transition in xanthates and dixanthogens. But a corresponding band is altogether absent in the latter compounds above $200\text{ m}\mu$. The intense band around $280\text{ m}\mu$, therefore, seems to be the characteristic feature of $\text{N}-\text{C}=\text{S}$ group because a similar band is present also in the other nitrogen containing thiones.²⁰

The intense band in the region $330-350\text{ m}\mu$ in the spectrum of potassium butyl trithiocarbonate (Fig. 5) is practically insensitive to solvents like water, alcohol and acetonitrile. A corresponding band is absent in the spectra of *S,S*-dibutyl dithiobis(dithioformate) (Fig. 6), dimethyl trithiocarbonate,¹⁹ and *S*-carboxy methyl trithiocarbonate¹⁹ while it is noticed in ethyl trithiocarbonic acid²² and sodium α -hydroxy ethyl trithiocarbonate.²³ It may be observed that this band appears only in salts or salt-like compounds and not in covalent compounds. The assignment of this band is difficult because of its insensitive nature to different solvents. It is likely that this band has merged with the $308\text{ m}\mu$ band in the covalent compounds.

The low wavelength intense band ($\log \epsilon \approx 4$) in thiuram disulphides, dixanthogens, and *S,S*-dibutyl dithiobis(dithioformate) occurs around 220 , 240 , and $260\text{ m}\mu$, respectively. This band shifts to shorter wavelengths in their respective alkali metal salts. Thus, in xanthates and trithiocarbonates the absorption maximum appears around 220 and $235\text{ m}\mu$, respectively, while in dithiocarbamates an end absorption suggests its presence below $200\text{ m}\mu$. The band shows mainly a blue shift when the solvent is changed from a non-polar to a polar one. The band, therefore, may be ascribed to $n \rightarrow \sigma^*$ transition. The $n \rightarrow \sigma^*$ transition can be explained by the excitation of an electron from the non-bonding lone pair of electrons, localized on the bonded sulphur atom in the $\text{S}-\text{S}$ group, to an antibonding orbital. The $n \rightarrow \sigma^*$ transition in the $\text{S}-\text{S}$ group is preferred by the present authors,¹⁵ by Mason²⁴ and by Bergson.²⁵ In his studies on the effect of sulphuric acid on the band in the region $225\text{ m}\mu$ for *S*-ethyl *O*-ethyl xanthate and similar esters of dithiocarbamic and trithiocarbonic acids, Janssen¹⁸ observed a blue shift to below $215\text{ m}\mu$, indicating $n \rightarrow \sigma^*$ transition. This supports the $n \rightarrow \sigma^*$ assignment for the low wavelength intense band in the derivatives of thiocarbonic acid.

Acknowledgements. The authors are thankful to Professor K. A. Jensen and Professor M. R. A. Rao for their keen interest in the work.

REFERENCES

1. Janssen, M. J., Balasubramanian, A. and Rao, C.N.R. *J. Sci. Ind. Res. (India)* **20 B** (1961) 349.
2. Rao, C.N.R., Balasubramanian, A. and Ramachandran, J. *Ibid.* **20 B** (1961) 382.
3. Balasubramanian, A. and Rao, C.N.R. *Spectrochim. Acta* **18** (1962) 1337.
4. Rosengren, K. *Acta Chem. Scand.* **16** (1962) 2284.
5. Sandström, J. *Ibid.* **16** (1962) 1616; **17** (1963) 678, 731, 931.
6. Fabian, J. and Mayer, R. *Spectrochim. Acta* **20** (1964) 299.
7. DeWitt, C. C. and Roper, E. E. *J. Am. Chem. Soc.* **54** (1932) 445.
8. Shankaranarayana, M. L. and Patel, C. C. *Analyst* **86** (1961) 98.
9. Whitby, G. S. and Greenberg, H. *Trans. Roy. Soc. Can. Sect. III* **23** (1929) 21.
10. Jensen, K. A. *J. prakt. Chem.* **159** (1941) 189.
11. Shankaranarayana, M. L. and Patel, C. C. *Anal. Chem.* **33** (1961) 1398.

12. Twiss, D. J. *Am. Chem. Soc.* **49** (1927) 491.
13. Grodzki, M. *Ber.* **14** (1881) 2754.
14. Weissberger, A., Proskauer, E. S., Riddick, J. A. and Toops, E. E., Jr. *Organic Solvents*, 2nd Ed. Interscience Publ., New York 1955, pp. 338 and 435.
15. Shankaranarayana, M. L. and Patel, C. C. *Can. J. Chem.* **39** (1961) 2590.
16. Kasha, M. *Discussions Faraday Soc.* **9** (1950) 14.
17. Sidman, J. W. *Chem. Rev.* **58** (1958) 689.
18. Janssen, M. J. *Rec. Trav. Chim.* **79** (1960) 454.
19. Janssen, M. J. *The Electronic Structure of Organic Thion Compounds*, Doctoral Thesis, Utrecht 1959.
20. Janssen, M. J. *Rec. Trav. Chim.* **79** (1960) 464, 1066.
21. Nagakura, S. *Bull. Chem. Soc. Japan* **25** (1952) 164.
22. von Halban, V., Mackert, A. and Ott, W. *Z. Electrochem.* **29** (1923) 445.
23. Barltrop, J. A., Hayes, P. N. and Calvin, M. J. *Am. Chem. Soc.* **76** (1954) 4357.
24. Mason, S. F. *Quart. Rev.* **52** (1963) 20.
25. Bergson, G. *Arkiv Kemi* **18** (1961) 409.

Received March 8, 1965.