

Localization of the C=S and the C—S Group Frequencies in Carboxymethyl Dithioesters

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Twenty-one carboxymethyl dithioesters were investigated spectrophotometrically in the infrared (400–4 000 cm^{-1}). Almost without exceptions intense bands were observed at 1 350–1 365, 1 290–1 325, 1 190–1 225, and 640–670 cm^{-1} . The bands close to 1 200 and 660 cm^{-1} were assigned to the C=S and the C—S stretching frequency modes.

The location of the C=S and the C—S group frequencies in organosulphur compounds has been a matter of considerable discussion. The literature concerned with this problem has lately been reviewed by Bellamy¹. Both group frequencies are difficult to localize because they, unlike *e. g.* the characteristic C—H, C=N, and C=O frequencies, fall in a spectral region where "fingerprint frequencies" are numerous. Valuable guidance as to their approximate position may, however, be obtained by a simplified force-constant calculation. From this it follows, that the two frequencies must be looked for in the vicinity of 1 200 cm^{-1} (C=S) and 700 cm^{-1} (C—S). Probably, therefore, the somewhat meager literature on the localization of the latter frequency is caused by the fact that the usual rock-salt optics does not allow observations below *ca.* 700 cm^{-1} . Since a number (21) of new carboxymethyl dithioesters were prepared in this laboratory² we decided to determine their infrared absorption spectra. All dithioesters should possess the two group frequencies we are looking for. Recently, Brader *et al.*³ have studied infrared spectra of a few (7) alkyl dithioesters. Tentatively they assigned the C=S frequency to 1 170–1 195 cm^{-1} for dithioesters but they were unable to identify the C—S frequency because of lack of KBr-optics. Felumb⁶ located the C=S group frequency in dixanthogenes to the 1 210–1 230 cm^{-1} region. Schotte⁷ has found the C—S group frequency in a series of dithiolane derivatives. Also, the paper by Mecke⁸ on thiocarbonyl compounds discusses the position of the C=S band.

Table 1. Schematic representation of infrared absorption spectra of 21 carboxymethyl
 Ordinate in mm = 1/10 of observed optical density per

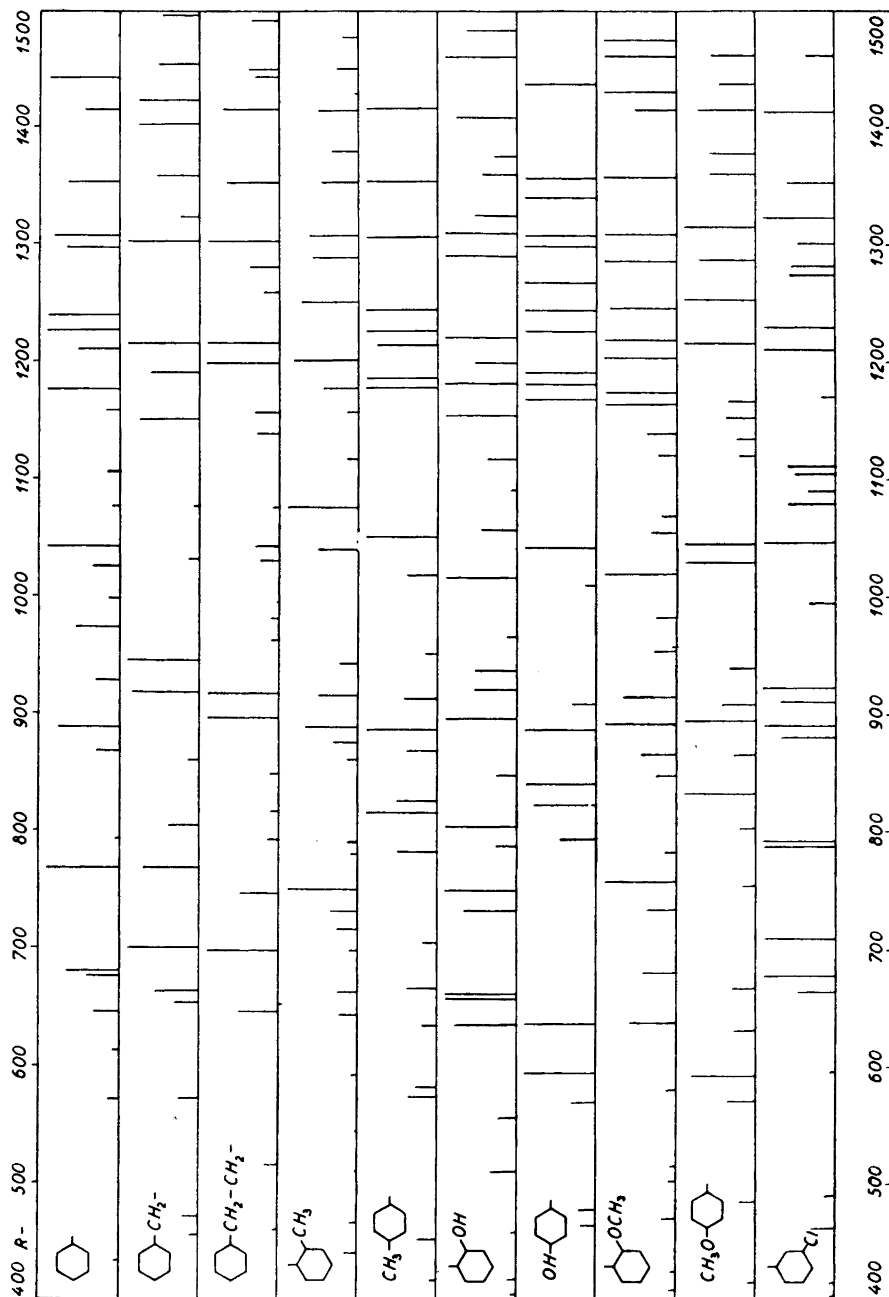


Table 1 (a)

dithioesters (R-CSSCH₂COOH). Abscissa: wavenumber of radiation (400–1 500 cm⁻¹), millimole if less than 100. Higher densities recorded as 10 mm.

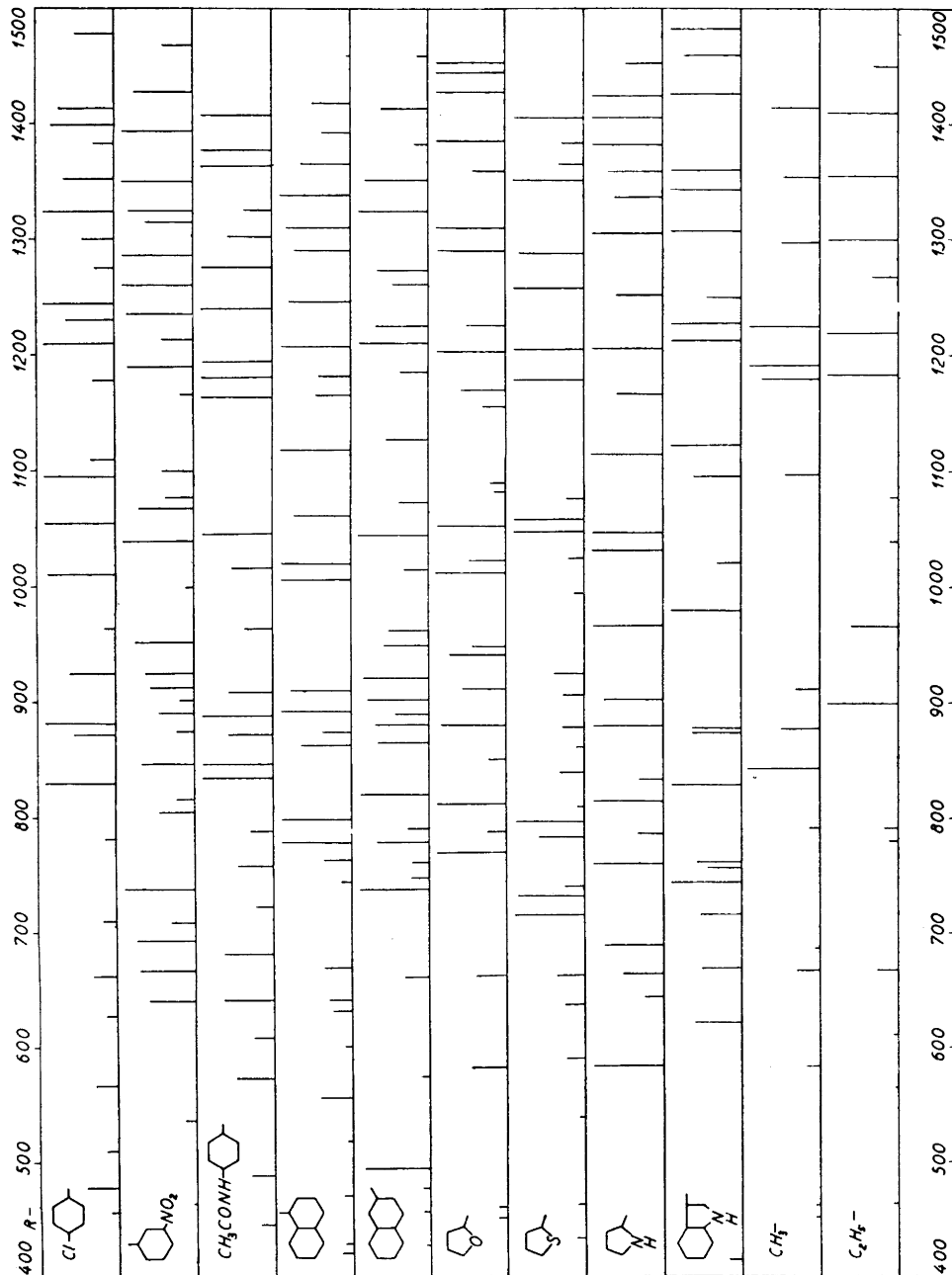


Table 1 (b)

EXPERIMENTAL

The spectra were obtained employing a Perkin-Elmer model 21 double beam infrared spectrophotometer equipped with NaCl, KBr, and CaF₂ optics. Since the compounds investigated are solids, KBr disk technique was applied (300 mg KBr mixed with 0.4–1.8 mg sample). The error in the frequency measurements is thought to be less than 2 cm⁻¹. For convenience the main features of the observed spectra are recorded graphically in Table 1. Although all the spectra were examined in the 400–4 000 cm⁻¹ region it was not found useful to include more than the 400–1 500 cm⁻¹ interval in Table 1. The spectra of all the compounds in question show, of course, the very broad and intense carboxyl band in the 2 400–3 400 cm⁻¹ region and the intense carbonyl band at 1 700–1 725 cm⁻¹, these bands are of little diagnostic value.

DISCUSSION

The analysis was started by localizing a number of group frequencies that must be present in the spectra of these compounds according to their composition (*e. g.* the CH₃-, the CH₂-, the C₆H₅-, and the OH-group frequencies). It was, *i. a.*, noted that the two low-frequency COOH-bands appeared rather persistently in the 1 400–1 425 cm⁻¹ and the 880–945 cm⁻¹ intervals.

Two other bands of rather constant frequency throughout the series were observed, *viz.* bands at 1 350–1 365 and 1 290–1 325 cm⁻¹. The present spectroscopic material is insufficient for an identification of the mechanical

Table 2. Observed optical densities per mmole (D_{obs}) for C=S and C-S group frequencies.

Radical R—	C=S		C-S	
	D_{obs} per mmole	Frequency	D_{obs} per mmole	Frequency
Phenyl-	113	1 226	45	667
Benzyl-	210	1 215	62	663
<i>a</i> -Phenylethyl-	240	1 215	56	661
<i>o</i> -Tolyl-	89	1 200	31	662
<i>p</i> -Tolyl-	110	1 225	44	666
<i>o</i> -Hydroxyphenyl-	210	1 219	118	662
<i>p</i> -Hydroxyphenyl-	350	1 225		
<i>o</i> -Methoxyphenyl-	260	1 218	13	670
<i>p</i> -Methoxyphenyl-	132	1 215	36	667
<i>m</i> -Chlorophenyl-	130	1 210	54	664
<i>p</i> -Chlorophenyl-	115	1 210	33	662
<i>m</i> -Nitrophenyl-	94	1 190	66 (79)	640 (667)
<i>p</i> -Acetamidophenyl-	230	1 194	71 (71)	640 (682)
<i>a</i> -Naphthyl-	110	1 207	41	670
<i>β</i> -Naphthyl-	120	1 210	37	662
2-Furyl-	175	1 203	46	663
2-Thenyl-	112	1 205	42	664
2-Pyrryl-	200	1 206	60	665
3-Indolyl-	294	1 213	57	670
Methyl-	130	1 225	34	668
Ethyl-	100	1 220	31	668

character of these modes of vibration. They must, however, somehow be characteristic for the $-\text{CSSCH}_2\text{COOH}$ grouping since the radicals attached to the group are rather different. Neither of the two bands can be attributed to the $\text{C}=\text{S}$ stretching vibration because of their position at too high a frequency.

Table 2 gives the observed optical density (D_{obs}) per mmole substance for bands in the $1\ 190\text{--}1\ 225\ \text{cm}^{-1}$ interval finally assigned as the $\text{C}=\text{S}$ stretching frequency, and for bands in the $640\text{--}670\ \text{cm}^{-1}$ interval assigned as the C—S stretching frequency.

The result fits well with the assignment given by Mecke and Spiesecke for CH_3CSSH ⁴. They found $\nu(\text{C}=\text{S}) = 1\ 216\ \text{cm}^{-1}$. Also there is substantial agreement with Sheppard's paper⁵ in which "primary" mercaptans, sulphides and disulphides all were shown to absorb in the $630\text{--}660\ \text{cm}^{-1}$ region.

The C—S band is, therefore, unobservable by means of the ordinary NaCl optics.

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