

Absorption Spectra of Alkyl *iso*Thiocyanates and N-Alkyl Monothiocarbamates*

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Ultra-violet absorption spectra of twenty-two *iso*thiocyanates and N-alkyl monothiocarbamates have been determined. Whereas the former class of substances invariably displays a maximum of moderate intensity ($\epsilon \sim 10^3$) in the 244–248 $m\mu$ region, the N-alkyl monothiocarbamates possess absorption bands in the range 226–232 $m\mu$ and an attempt has been made to correlate the wave-length position of the absorption maximum with the structure of the substituents.

In the infra-red range of the spectrum, alkyl *iso*thiocyanates exhibit characteristic bands in two regions. The asymmetric stretching mode of the cumulative double bond system of the $-N=C=S$ -grouping produces a moderately intense band at 2 170–2 221 cm^{-1} , accompanied by a group of two to three strong bands at 2 050–2 150 cm^{-1} , as well as a very weak band in the 2 000 cm^{-1} region. The position and intensity of the bands depend on the polarity of the solvents employed. The second characteristic frequency of alkyl *iso*thiocyanates occurs at 1 318–1 347 cm^{-1} and is assigned to the bending vibrations of $-CH_2$ -atoms adjacent to the $-N=C=S$ -grouping. This very strong band has been observed in all compounds possessing the $RCH_2-N=C=S$ grouping, whereas methyl, *tert.*-butyl, phenyl and α -naphthyl *iso*thiocyanates do not exhibit typical absorption in the vicinity of 1 330 cm^{-1} .

The electronic spectra of alkyl *iso*thiocyanates have attracted only little attention heretofore. Kremann and Riebl¹ determined the absorption curve of allyl *iso*thiocyanate, whereas Pestemer and Litschauer² in addition to this mustard oil studied the spectroscopical properties of the ethyl- and monomethoxy-derivatives. According to these authors, *iso*thiocyanates possess absorption maxima at approximately 250 $m\mu$ with $\log \epsilon \sim 3$. Although the absorption properties of N-alkyl monothiocarbamates in the ultra-violet region have been utilized analytically they do not seem to have been subjected to detailed studies previously.

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There does not exist any comprehensive treatise of the infra-red spectra of alkyl *isothiocyanates*. The first data on the frequencies characteristic for such compounds were presented by Coblenz³ who studied methyl, ethyl, allyl and phenyl *isothiocyanate*. In view of the imperfect technique used in 1905, however, these frequencies can hardly be considered as too reliable. Gordy and Williams⁴ later reported methyl and ethyl *isothiocyanate* to possess bands at (3 012 cm⁻¹, 2 127 cm⁻¹) and (3 039 cm⁻¹, 2 205 cm⁻¹), respectively. Williams⁵ recorded frequencies of the phenyl *isothiocyanate* bands in the 650—3 000 cm⁻¹ range but paid particular attention to the vibration of the —N=C=S-grouping, which displayed a broad band at 2 100 cm⁻¹. This consists, according to geometrical analysis, of three bands at 2 130, 2 080 and 1 950 cm⁻¹. As an explanation of this phenomenon the author considered Fermi resonance of the —N=C=S-group vibration, accompanied by an overtone of the fundamental frequency at 685 cm⁻¹.

More recently, frequency values of some *isothiocyanates* have been listed in the papers by Ettlinger *et al.* (3-butenyl, *trans*- and *cis*-crotyl⁶, *m*-methoxybenzyl⁷), Kjær and colleagues (*trans*-crotyl⁸, *p*-methoxybenzyl⁹ and *o*-methoxybenzyl¹⁰) and Luskin *et al.*¹¹ The last authors summarized previous data and quoted the range 2 040—2 180 cm⁻¹ for the strong NCS-group absorption. On basis of own experiments they concluded that *isothiocyanates* in carbon tetrachloride solution display a strong band at 2 095 ± 15 cm⁻¹, frequently accompanied by a weak band at 2 000 cm⁻¹.

Attention should be drawn also to the Raman spectra of *isothiocyanates*. In these, two especially intensive lines were observed at 2 100 and 2 170 cm⁻¹, both attributable to the —N=C=S group, rather than the expected single line^{12,13}. Bagder¹⁴ explained this doubling of the line of the —N=C=S mode in terms of Fermi resonance of the —N=C=S vibration with an overtone of the fundamental line at 1 070 cm⁻¹. This explanation, however, was later criticized by Kohlrausch¹³ because it only applies in some cases (methyl and ethyl *isothiocyanate*), whereas it does not hold for other derivatives. On basis of the Raman spectra a strong contribution of the mesomeric structure

$\text{R}-\overset{\oplus}{\text{N}} \equiv \text{C}-\overset{\ominus}{\text{S}}$ to the *isothiocyanate* structure has been suggested.

The present paper records the results from investigations of the absorption spectra of a series of alkyl *isothiocyanates* and N-alkyl monothiocarbamates in the ultra-violet region between 220 and 350 m μ . It further presents the infra-red spectra of twenty-two *isothiocyanates* in the region of the —N=C=S vibration (2 100 cm⁻¹). Of these, twelve selected species were further studied in the 1 600—650 cm⁻¹ region where the —N=C=S grouping has not formerly been characterized.

EXPERIMENTAL

Apparatus and methods. Absorption curves in the ultra-violet region^r were recorded with the Soviet spectrophotometer SF 4 at 21 ± 2°. All solutions were measured in 1.00 cm cells. The concentrations employed were usually 10⁻³ M or 10⁻⁴ M, depending on whether *isothiocyanates* or N-substituted monothiocarbamates were being examined. Extinction readings were taken with 1 m μ intervals in the vicinity of absorption maxima, otherwise in steps of 5 m μ . Wave-length values were controlled by a mercury lamp and

are regarded as accurate within $\pm 0.5 m\mu$ in the $250 m\mu$ region. Extinction values are considered accurate to $\pm 3\%$. Most absorption curves of alkyl isothiocyanates were recorded in dioxane solution, whereas samples of the N-alkyl monothiocarbamates were prepared *in situ* by allowing such an amount of alkyl isothiocyanate to react with 0.1 N NaOH that the resulting solution became 10^{-4} M. Four hours later, the absorption curves of the N-alkyl monothiocarbamates, resulting from the reaction of alkyl isothiocyanates with the OH-ions¹⁵, were determined. At the end of this time, the reaction had proceeded virtually to completion in all cases except when the slower reacting *tert.*-butyl isothiocyanate was employed.

Infra-red spectra were determined with a Perkin-Elmer Model 12 B single-beam spectrophotometer with rock salt optics, and with a Zeiss Jena UR 10 double-beam spectrophotometer equipped with a lithium fluoride prism (for the range $1900-2300 \text{ cm}^{-1}$). The accuracy of frequencies in well-developed bands is $\pm 1 \text{ cm}^{-1}$. The instrument was calibrated against ammonia, atmospheric water and carbon dioxide, as well as polystyrene, benzene, pyridine and chloroform. The spectra were registered at constant temperature (25°), maintained by a room thermostat.

Reagents. The alkyl isothiocyanates examined were the same substances as those studied in a preceding paper¹⁵. Dioxane (Lachema, reagent grade) was refluxed prior to use with a tenth of a volume of 4% hydrochloric acid in a stream of nitrogen. Water and hydrochloric acid were then removed by shaking with solid potassium hydroxide. Thereafter, the dioxane was boiled for 9 h with metallic sodium, the precipitate and excess sodium were removed and the product distilled over fresh sodium. The main run was used in the experiments. Every third day, the dioxane was redistilled over sodium and the solvent was stored in the solid state in a refrigerator.

Other solvents employed were purified by standard procedures. All materials used were of reagent grade purity (Lachema).

RESULTS

Ultra-violet spectra of alkyl isothiocyanates and N-alkyl monothiocarbamates. In the region of electronic spectra alkyl isothiocyanates are characterized by a single absorption band of medium intensity ($\epsilon \sim 10^3$) possessing a maximum between 244 and $248 m\mu$. Absorption curves of all mustard oils examined display the same general pattern, exemplified by the absorption curve (No. 1)

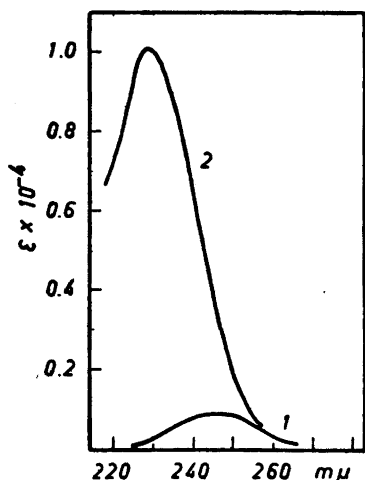


Fig. 1. The molecular extinction coefficient (ϵ) as a function of the wave-length. 1. cyclohexyl isothiocyanate in dioxane; 2. N-cyclohexyl monothiocarbamate in 0.1 M NaOH.

Table 1. Absorption data for ethyl *iso*thiocyanate (0.001 M solutions) in various solvents.

	Pentane 95 % Dioxane 5 %	Chloroform 90 % Dioxane 10 %	Dioxane	0.05 M HCl 50 % (aqueous) Ethanol 40 % Dioxane 10 %
λ_{\max} (m μ)	250	245	245	241
log ϵ	2.94	2.86	2.86	2.82

Table 2. Position and intensity of ultra-violet absorption maxima of alkyl *iso*thiocyanates and N-alkyl monothiocarbamates.

No.	Alkyl R	Number of α -substituents	<i>iso</i> Thiocyanates: R—NCS ^a			Monothiocarbamates: R—NH—COS ^{⊖f}		
			$\Delta\lambda_{\max}$, Et ^b	$\Delta\lambda_{\max}$, Al ^c	log ϵ	$\Delta\lambda_{\max}$, Et ^b	$\Delta\lambda_{\max}$, Al ^c	log ϵ
I	Methyl	0	—1		2.8	—1		4.0
II	Ethyl	1	0 ^d		2.9	0 ^g		4.0
III	<i>iso</i> Propyl	2	1		2.90	2		3.9
IV	<i>tert.</i> -Butyl	3	3		3.05	6		—
V	<i>iso</i> Butyl	1	0		2.86	0		3.9
VI	<i>n</i> -Butyl	1	0		2.85	0.5		4.0
VII	<i>n</i> -Amyl	1	0		2.83	0.5		4.0
VIII	<i>n</i> -Hexyl	1	0		2.78	0.5		4.0
IX	<i>n</i> -Octyl	1	0		2.94	0.5		4.0
X	<i>cyclo</i> Hexyl	2	1.5		2.94	3		4.0
XI	Allyl	1	1	0 ^e	2.94	1	0 ^h	4.1
XII	DL- α - Methallyl	2	3	2	2.98	2	1	4.0
XIII	β -Methallyl	1	2	1	2.97	1	0	4.0
XIV	<i>trans</i> -Crotyl	1	1.5	0.5	3.04	1	0	4.1
XV	3-Butenyl	1	1	0	2.94	1	0	4.0
XVI	4-Pentenyl	1	0	—1	2.85	0	—1	4.0
XVII	Benzyl	1	3	2	3.08	3	2	4.1
XVIII	DL- α - Phenethyl	2	2.5	1.5	3.19	2	1	4.0
XIX	3-Methyl- thiopropyl	1	0.5		3.01	0		4.1
XX	4-Methyl- thiobutyl	1	0		2.98	0		4.0
XXI	5-Methyl- thiopentyl	1	0		2.97	0		4.0
XXII	Phenyl	1	25		3.98	32		4.2

^a Measured in 10⁻³ M solutions in dioxane. ^b The relative absorption maxima $\Delta\lambda_{\max}$, Et = $\lambda_{\max, i} - \lambda_{\max, Et}$, where $\lambda_{\max, i}$ is the position of the absorption maximum of the *i*th derivative and $\lambda_{\max, Et}$ is a similar symbol for the reference derivative (ethyl). ^c The same symbol as defined for ^b, yet with the allyl derivative as the reference compound. ^d λ_{\max} (ethyl) = 245 m μ ; ^e λ_{\max} (allyl) = 246 m μ ; ^f Measured in 10⁻⁴ M solution in 0.1 N NaOH; ^g λ_{\max} (ethyl) = 226 m μ . ^h λ_{\max} (allyl) = 227 m μ .

of Fig. 1. The influence of solvent composition was investigated in the case of ethyl isothiocyanate (Table 1). The position and intensity of the absorption maxima of all species studied are summarized in Table 2.

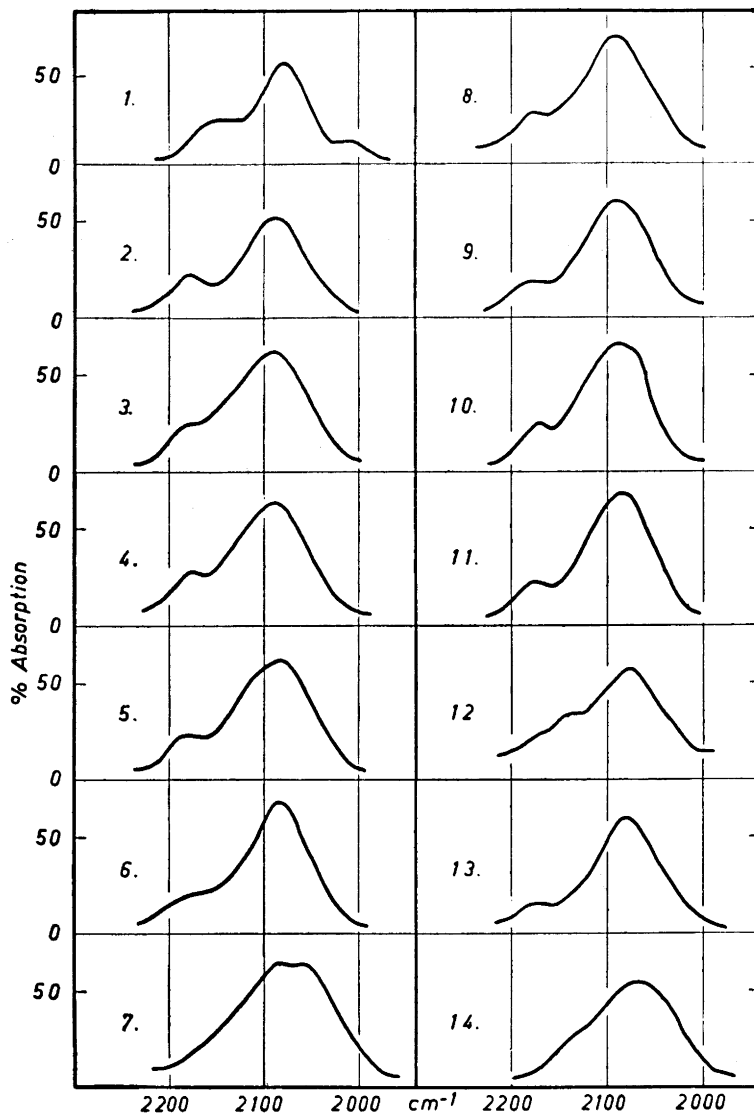


Fig. 2. Infra-red absorption bands of various isothiocyanates in the 1 900–2 300 cm^{-1} region. (The thickness of the cell is 0.10 mm, concentration: 0.1 M in CCl_4 , sodium chloride prism). 1. *iso*Propyl-, 2. *isobutyl*-, 3. *n*-hexyl-, 4. *n*-amyl-, 5. *iso*amyl-, 6. β -methallyl-, 7. DL- α -methallyl-, 8. *n*-octyl-, 9. 3-methylthiopropyl-, 10. 4-methylthiobutyl-, 11. 3-butenyl-, 12. *trans*-crotyl-, 13. benzyl-, 14. DL- α -phenethyl-isothiocyanate.

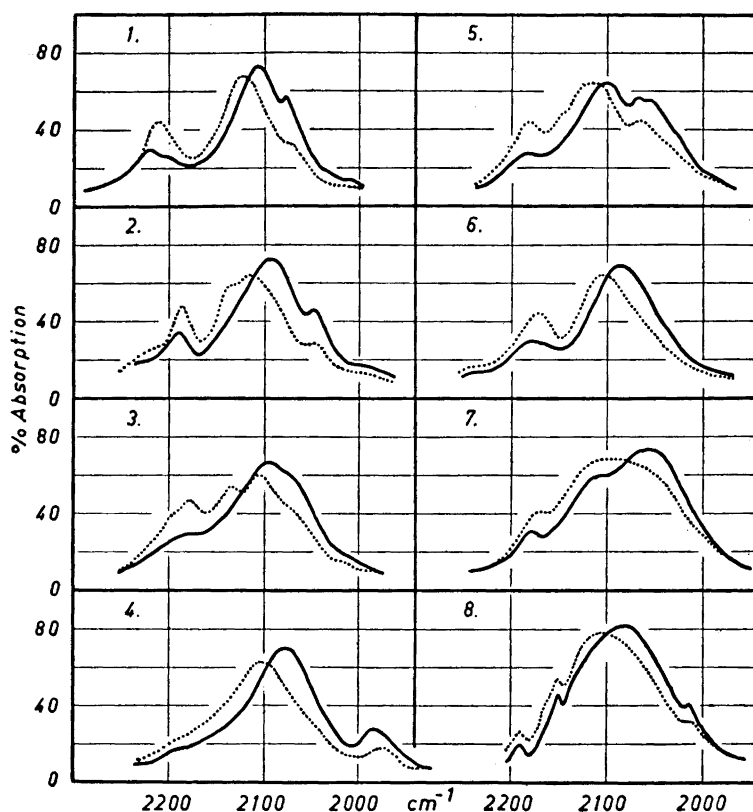


Fig. 3. Infra-red absorption bands of various *isothiocyanates* in the 1900–2300 cm^{-1} region. (Concentration 0.1 M; in CCl_4 -solution: full line; in CHCl_3 : dotted line; absorption cell 0.10 mm, lithium fluoride prism). 1. Methyl-, 2. ethyl-, 3. *n*-butyl-, 4. *tert.*butyl-, 5. cyclohexyl-, 6. allyl-, 7. phenyl-, 8. α -naphthyl- *isothiocyanate*.

The general shape of the absorption curves of N-alkyl monothiocarbamates are similar to those of the mustard oils except for their higher intensity of the maximum absorption bands ($\epsilon \sim 10^4$) (cf. Fig. 1, curve 2) which are located between 226 and 232 μ (Table 2).

Infrared spectra of alkyl *isothiocyanates*

The 1900–2300 cm^{-1} region. In this region the spectra of twenty-two different *isothiocyanates* were measured in carbon tetrachloride solution (0.1 M) in an 0.1 mm absorption cell (sodium chloride prism). Within this group, eight selected compounds were studied under comparable conditions at the higher resolving power of a lithium fluoride prism, and, in addition, in chloroform solution. Spectra of ethyl *isothiocyanate* were recorded also

Table 3. Position (cm^{-1}) and intensity (% absorption) of bands of the $-\text{N}=\text{C}=\text{S}$ -grouping in the $1\,900\text{--}2\,300\text{ cm}^{-1}$ region. (Concentration 0.1 M. (a): in CCl_4 ; (b): in CHCl_3 . Thickness of the absorption cell 0.10 mm, lithium fluoride prism.)

Substituent	cm^{-1}	% A	cm^{-1}	% A	cm^{-1}	% A	cm^{-1}	% A	cm^{-1}	% A	Solvent
Methyl	2 221	30			2 106	74	2 077	56			a
	2 210	44			2 123	67	2 071	31			b
Ethyl	2 187	34			2 092	73	2 049	45			a
	2 184	47	2 135	58	2 113	63	2 046	28			b
<i>n</i> -Butyl	2 173	30 (i)*			2 097	66	2 068	56 (i)			a
	2 178	47	2 135	54	2 105	60	2 068	40 (i)			b
Allyl	2 172	31			2 087	68	2 072	63 (i)			a
	2 170	44			2 103	64	2 070	?			b
<i>cyclo</i> Hexyl	2 180	28			2 100	64	2 053	54			a
							2 067	56			a
	2 182	43	2 148	? (i)	2 113	63	2 064	44			b
<i>tert.</i> -Butyl					2 079	72			1 982	29	a
					2 104	64			1 976	19	b
Phenyl	2 177	30			2 106	60	2 054	74			a
	2 168	40			(2 100)	66	2 065	64			b
α -Naphthyl	2 190	20	2 150	45	2 080	82			2 015	41	a
	2 190	26	2 150	54	2 105	78			2 015	32	b

* (i): inflection.

in two extreme concentrations, *viz.* 0.01 M (1 mm cell) and 1.00 M (0.03 mm cell), as well as in the undiluted liquid and vaporous phase. The experimental curves are presented in Figs. 2 and 3, and the main frequencies and absorption data of eight selected compounds are reviewed in Table 3.

A typical feature of all the above compounds is the appearance of three to four bands which can be well differentiated: (i) a band of medium intensity in the $2\,170\text{--}2\,221\text{ cm}^{-1}$ region, (ii) a group of two to three strong bands in the range $2\,050\text{--}2\,150\text{ cm}^{-1}$, and (iii) a weak band around $2\,000\text{ cm}^{-1}$ which, in most cases, is poorly distinguishable and hence has not been studied in detail.

In chloroform solution a striking change of band intensities was observed on comparison with experiments where carbon tetrachloride served as the solvent. The band at $2\,170\text{--}2\,221\text{ cm}^{-1}$ rose at the expense of that located at $2\,050\text{--}2\,080\text{ cm}^{-1}$ whereas the strong band at $2\,100\text{ cm}^{-1}$ was displaced towards higher wave-numbers ($\Delta\nu \sim 20\text{ cm}^{-1}$) and slightly decreased in intensity. The total band intensity, however, expressed as $\int A\,d\nu$ (the area of all bands from $1\,950\text{ cm}^{-1}$ through $2\,350\text{ cm}^{-1}$), remained the same in carbon tetrachloride and chloroform.

In the above-mentioned region the spectra of the whole series of mustard oils are essentially identical, yet with three striking exceptions, *viz.* methyl, *tert.*-butyl and phenyl isothiocyanate. Among all compounds examined, the methyl derivative displays bands at the highest frequencies. Tertiary butyl isothiocyanate is devoid of any maximum in the $2\,180\text{ cm}^{-1}$ region (in chloroform a shoulder only), but displays a maximum at $1\,985\text{ cm}^{-1}$. Finally, phenyl

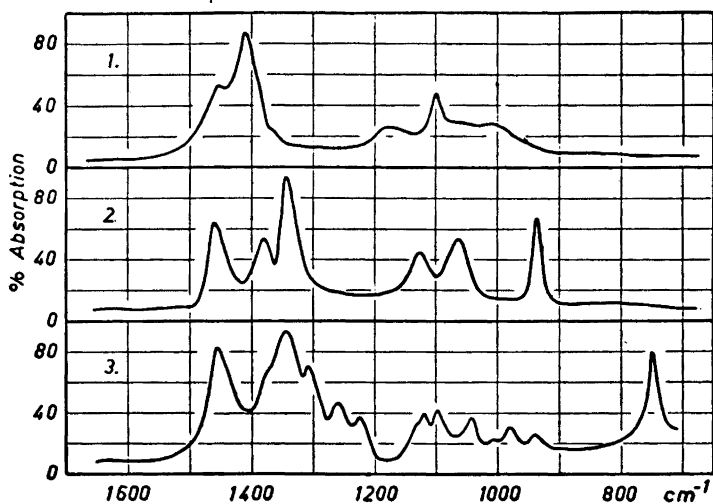


Fig. 4. Infra-red spectra of various *isothiocyanates*. (5 % solutions in CCl_4 or CS_2).
1. Methyl *isothiocyanate*. 2. Ethyl *isothiocyanate*. 3. *n*-Butyl *isothiocyanate*.

isothiocyanate has its predominant bands at $2\,054\text{ cm}^{-1}$ (in CCl_4) and also absorbs most intensely of all compounds listed in Table 3 in terms of $\int A\,d\nu$.

Ethyl *isothiocyanate*, a typical representative of the present series, served as a model compound for the study of the dependence of the position and intensity of absorption bands on concentration, in carbon tetrachloride as

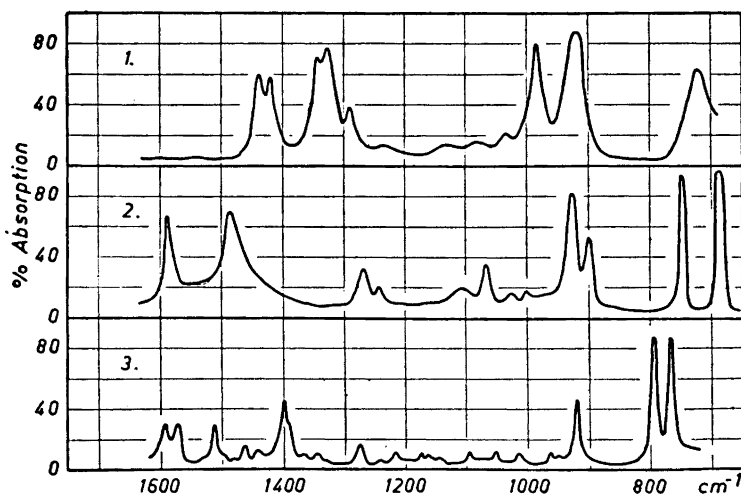


Fig. 5. Infra-red spectra of various *isothiocyanates* (5 % solutions in CCl_4 or CS_2).
1. Allyl *isothiocyanate*. 2. Phenyl *isothiocyanate*. 3. α -Naphthyl *isothiocyanate*.

well as chloroform. No conspicuous changes were noted, however. The spectra of the ethyl derivative as a film (liquid state) and in the vaporous phase did not deviate from those determined in solution.

The 1 800—1 500 cm^{-1} region. In this "double bond range" we have found no bands in the alkyl isothiocyanates. Only derivatives of unsaturated alkyls and aromatic derivatives display absorption in agreement with literature assignments¹⁸.

The 1 500—650 cm^{-1} region. Some typical regularities characteristic for the presence of the $-\text{N}=\text{C}=\text{S}$ grouping were observed in this spectral range (Figs. 4 and 5). In the homologous series of normal substituents from ethyl to *n*-octyl, a strong absorption band at 1 346—1 348 cm^{-1} was apparent (ethyl 1 346 cm^{-1} , *n*-butyl 1 347 cm^{-1} , *n*-amyl 1 347 cm^{-1} , *n*-hexyl 1 348 cm^{-1} , *n*-octyl 1 347 cm^{-1}). Similarly, the allyl and benzyl derivatives displayed a band at 1 345 and 1 347 cm^{-1} , respectively. In *isopropyl* and *cyclohexyl isothiocyanate* the position of this band shifted to 1 329 and 1 318 cm^{-1} . Methyl, *tert.*-butyl, phenyl and α -naphthyl mustard oil again showed anomalous behaviour in this region compared with other compounds. None of them absorbed in the 1 350—1 300 cm^{-1} range, whereas methyl isothiocyanate exhibited an intensive band at 1 412 cm^{-1} and the *tert.*-butyl derivative at 1 205 cm^{-1} . The position of the 1 347 cm^{-1} -band appeared to be independent of the polarity of the solvent and the concentration.

DISCUSSION

Ultra-violet spectra

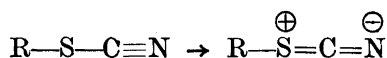
The molecular extinctions of the absorption maxima of alkyl isothiocyanates (244—248 $\text{m}\mu$) are approximately 10^3 , a value intermediate between those characteristic for allowed and forbidden transitions. For the following reasons we believe that the absorption is assignable to the allowed $\text{N} \rightarrow \text{V}$ transition. An analysis of Raman as well as infra-red spectra suggests that the electron distribution in the NCS-grouping is approximately that of the dipolar form

$\overset{\oplus}{\text{R}}-\overset{\ominus}{\text{N}}\equiv\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{S}}$. The only likely $\text{N} \rightarrow \text{V}$ -transition in the present structure, however, is associated with the creation of cumulated double bonds

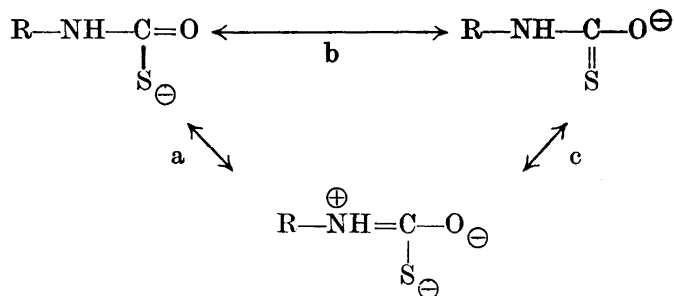
$\overset{\oplus}{\text{R}}-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}}-\overset{\ominus}{\text{S}} \rightarrow \overset{\oplus}{\text{R}}-\overset{\oplus}{\text{N}}=\overset{\ominus}{\text{C}}=\overset{\ominus}{\text{S}}$ and such transitions are known to result in rather low extinction values¹⁶. The occurrence of an $\text{N} \rightarrow \text{V}$ -transition in the present case is supported also by the position of the absorption maximum. The range 245—260 $\text{m}\mu$ can be considered as the customary location for absorption bands attributable to transitions of the present type.

In this connexion attention should be drawn to the ultra-violet spectrum of the isomeric alkyl thiocyanates which exhibit² an absorption maximum of weak intensity ($\epsilon = 30$) in the 240 $\text{m}\mu$ region, apparently belonging to a forbidden transition. This deviating pattern is not unexpected because the electron shift, characteristic for the $\text{N} \rightarrow \text{V}$ -transition, in this case would

imply not only the formation of cumulated double bonds but also, and more importantly, the participation of a polar ion containing trivalent sulphur.



The situation is more complicated in the N-alkyl monothiocarbamate series because three significant N → V transitions can be visualized in molecules of this type, *viz.*:



It may be of interest to attempt an assignment of the absorption band ($\lambda = 226\text{--}232 \text{ m}\mu$) of high intensity ($\epsilon \sim 10^4$), characteristic for alkyl monothiocarbamates, to one of these transitions (a, b, c). That represented by (a) is not active in the near ultra-violet region, as can be inferred, *inter alia*, from the insignificant absorption of N-alkyl carbamates in the 220—400 $\text{m}\mu$ region. Comparison of the position of the absorption maximum of N-alkyl monothiocarbamates with that of compounds containing N—C=S groupings (Fig. 6) suggests that the absorption maximum of the monothiocarbamates should be attributed to the transition (b) above. This interpretation, however, does not account for the fact that N-alkyl monothiocarbamates do not exhibit an additional maximum in the 245—260 $\text{m}\mu$ range, expectable from the transition (c) above. This is surprising, particularly because the formally similar dithiocarbamates and xanthogenates display maxima ascribable to the CSS- as well as to the N—C=S- or O—C=S-groupings.

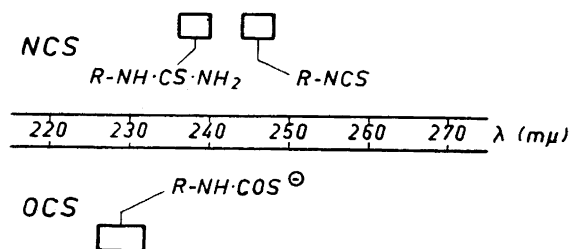
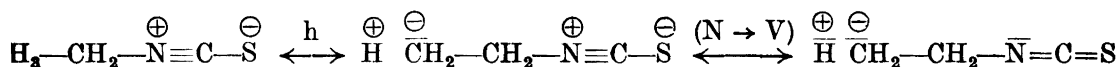


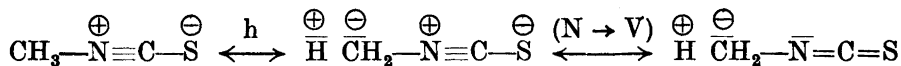
Fig. 6. Absorption maxima ranges of the —NCS and —OCS groupings in the ultra-violet region.

Influence of the structure of the R-group of isothiocyanates and monothio-carbamates on the position of the absorption maximum. From Table 2 it can be seen that the introduction of any substituent in the methyl derivative in both series results in a bathochromic shift of the absorption maximum. This means that groups characterized by an $-I_s$ effect (e.g. allyl, benzyl, phenyl) as well as those displaying an $+I_s$ effect (e.g. *tert.*-butyl) displace the absorption maximum towards higher wave-lengths, i.e. the $N \rightarrow V$ -transition associated with the appearance of the absorption band requires lower energy. As both types of substituents ($+I_s$, $-I_s$) produce a qualitatively similar shift, we conclude that the extension of conjugation (due to hyperconjugation) is responsible, rather than the inductive effect. The data in Table 2 disclose the fact that replacing of the first hydrogen of the methyl grouping results in a shift of $1 \text{ m}\mu$, whereas substitutions of the second and third hydrogens cause displacements of $2\text{-}4 \text{ m}\mu$. Substitution at the β - and γ -carbon atom is not reflected by changes of absorption maxima, but in the case of "medium-size" *n*-alkyls (C_5 , C_6 , C_8) a shift of $1 \text{ m}\mu$ relative to the ethyl derivative was noticed in the monothiocarbamate series. In the isothiocyanates these derivatives do not differ from the ethyl compound.

In the mustard oil series we consider hyperconjugation to be involved:



where h indicates a hyperconjugation displacement. Further substitution at the α -carbon atom of the ethyl derivative facilitates an extension of conjugation, whereas hyperconjugation in the methyl derivative operates less favourably, resulting in cumulation rather than conjugation of p electrons:



In both series, the ω -methylthioalkyl derivatives (XIX, XX and XXI) are closely comparable to the ethyl compound.

Apart from the number of substituents on the α -carbon atom (Table 2), the presence of π -electronic bonds in the substituting groups influences the magnitude of the bathochromic shift. Introduction of a double bond in β, γ -position (allyl derivatives) results in a shift equivalent to that produced by substitution of a hydrogen atom in the methyl derivative by a methyl grouping. Whereas in *N*-methallyl monothiocarbamate substitution at the α -carbon atom exclusively causes a bathochromic shift, the corresponding methallyl isothiocyanate is changed by β -substitution as well. In the α -substituted mustard oil (XII) this displacement amounts to $3 \text{ m}\mu$, which is more than the added influences of the allyl- ($1 \text{ m}\mu$) and the methyl-grouping ($1 \text{ m}\mu$) (estimated from the displacement on going from ethyl to *isopropyl isothiocyanate*). However, considering the error attached to these measurements this difference does not warrant a more detailed discussion. It is interesting that the presence of a γ, δ -double bond, as in (XV), in both series produces an effect comparable to that observable in the allyl series. Previous examples of a corres-

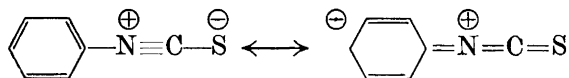
res a different slope, a deviation paralleling that observed in studies of the relative reaction velocities of alkyl isothiocyanates.

Infrared spectra

The 1 900—2 300 cm⁻¹ region. In this wave-length region an increase of the absorption band at about 2 180 cm⁻¹, accompanied by an intensity decrease of the 2 090 cm⁻¹ peak, is consistently observed on changing the solvent from CCl₄ to CHCl₃ (Fig. 3). The effect is presumably ascribable to an enhanced polarization of the NCS-grouping in the more polar solvent. The lacking band around 2 180 cm⁻¹ in the spectrum of *tert.*-butyl isothiocyanate (Fig. 3) is probably caused by steric influences.

The multiplet character of the band in this spectral region, attributed to the asymmetric stretching vibration of the —N=C=S grouping, is difficult to explain, for reasons similar to those outlined in the case of the Raman spectra¹³. Supplementary investigations of the Raman spectra are planned in order to clarify this problem. Association effects can hardly be responsible for the doubling of the bands, in view of the spectral independence of concentration or phase condition. Again, such phenomenons as tautomerism, hydrogen bonding or rotational isomerism seem very unlikely in case of the NCS-grouping.

The displacement of the absorption band from 2 100 cm⁻¹ to 2 054 cm⁻¹ in phenyl isothiocyanate (Fig. 3) is explainable in terms of a conjugation effect diminishing the contribution from the triple-bonded hybride to the molecule which is assumed to be planar:



A qualitatively similar but less pronounced displacement is observable in the spectrum of α -naphthyl isothiocyanate (Fig. 3), as would be expected.

The 1 500—650 cm⁻¹ region. A strong band at 1 348—1 318 cm⁻¹ can be assigned to the —CH₂N=C=S or >CH—N=C=S groupings. In the given region there has not been described, thus far, any intense, characteristic frequencies. Weak C—H-deformation modes (wagging and twisting) reaching into the 1 300 cm⁻¹ region, such as those operating here, have received only little attention, particularly regarding the influence of substituents. The symmetric stretching vibration of the —N=C=S-grouping, which in Raman spectra gives rise to a strong line at 1 070 cm⁻¹ (methyl and ethyl mustard oil) is, according to our findings, inactive or slightly active in the infra-red spectra examined. The strong band at 1 348—1 318 cm⁻¹ can hardly be assigned to the symmetric stretching mode of the —N=C=S grouping, since methyl, *tert.*-butyl, phenyl and α -naphthyl isothiocyanate do not absorb in this region. Furthermore, the Raman spectrum displays, in addition to the symmetric stretching vibration of the —N=C=S grouping at 1 070 cm⁻¹, a relatively strong line (in the ethyl derivative) of non-identified origin in the same region (1 340 cm⁻¹) where we find the band in the infra-red spectrum. It

is highly improbable that the stretching mode would be susceptible to that extent to the influence of substituents and be displaced only in methyl, *tert.*-butyl, phenyl and α -naphthyl *isothiocyanate* from 1 340 cm^{-1} to another region. The most plausible interpretation of the latter bond is therefore that it represents a deformation vibration of the C—H grouping, the force constant of

which is influenced by the presence of the polar $\text{—N}^{\oplus}=\text{C}^{\ominus}\text{—S}$ -grouping. A more exact characterization of the vibrational type would require a study of further derivatives. The introduction of deuterium to furnish the $\text{—CD}_2\text{—N}^{\oplus}=\text{C}^{\ominus}\text{—S}$ -grouping would, of course, be advantageous in such investigations.

Methyl *isothiocyanate* displays a strong band at 1 412 cm^{-1} , representing the symmetric deformation vibration of the methyl group and displaced by the influence of the $\text{—N}^{\oplus}=\text{C}^{\ominus}\text{—S}$ -grouping from its normal position at 1 380 cm^{-1} in the linear aliphatic chain. Corresponding shifts of the methyl grouping, conditioned by the influence of polar substituents, have been reported and studied in detail¹⁹⁻²¹. The band at 1 453 cm^{-1} represents the asymmetric deformation vibration of the methyl group, practically unaffected by the —NCS -substitution (normal position: 1 450 cm^{-1}).

Tertiary butyl *isothiocyanate* exhibits a broad, strikingly high band at 1 205 cm^{-1} within the region of the characteristic frequency of the *tert.* butyl-grouping. The intensity is probably influenced by the NCS-substitution.

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