

## CONFORMATIONAL STUDIES OF ESTERS OF 2-ISOTHIOCYANATO CARBOXYLIC ACIDS BY IR AND $^1\text{H-NMR}$ SPECTROSCOPY\*

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The effect of solvent on the  $\nu_{\text{as}}(\text{NCS})$  and  $\nu(\text{C}=\text{O})$  bands, and the effects of temperature and concentration on the chemical shifts of the protons in eleven alkyl 2-isothiocyanato and  $\omega$ -isothiocyanato carboxylates were investigated.

It is generally known that study of solvent effects enables assignment of infrared bands to the corresponding types of vibrations<sup>1,2</sup>. The solvent effect can be used in the study of tautomerism<sup>3</sup>, conformation<sup>4</sup>, hydrogen bonds<sup>5</sup>, Fermi resonance<sup>6</sup>, as well as in the determination of carbonyl groups in organic molecules<sup>7,8</sup>.

The shifts of bands owing to  $\sigma$ -bonds, caused by the change in the nature of the solvent, are relatively small, except shifts of the bands owing to bonds to atoms engaged in hydrogen bonding. On the other hand, the solvent shifts of the bands owing to  $\pi$ -bonds are much greater<sup>9</sup>. In proton donating solvents  $\nu(\text{C}=\text{O})$  bands are shifted to lower wavenumbers<sup>10</sup> whereas  $\nu_{\text{as}}(\text{NCS})$  bands are shifted to higher wavenumbers<sup>11,12</sup>. It has been found that proton donating, as well as proton accepting solvents cause a shift of  $\nu_{\text{as}}(\text{NCS})$  bands. On passing from tetrachloromethane to chloroform solution the wavenumber of the main  $\nu_{\text{as}}(\text{NCS})$  band at about  $2000\text{ cm}^{-1}$  increases by  $15\text{--}21\text{ cm}^{-1}$  in aliphatic<sup>13</sup> and by  $40\text{--}50\text{ cm}^{-1}$  in aromatic isothiocyanates<sup>11</sup>, whereas the second band is shifted to lower wavenumbers. With increasing polarity of the solvent the extinction coefficient of the  $\nu_{\text{as}}(\text{NCS})$  band decreases. The half-widths of the bands in the spectra of aromatic isothiocyanates are about  $20\text{ cm}^{-1}$  greater than those in aliphatic isothiocyanates<sup>11</sup>.

The  $^1\text{H-NMR}$  spectrum of a compound which exists in two comparably populated conformations corresponds either to these two individual conformations, or shows an average spectrum which can split at a low enough temperature into two separate sets of signals<sup>14,15</sup>. The temperature dependence of the chemical shift in isothio-

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cyanates was hitherto not studied. In our previous paper<sup>1</sup> we concluded on the basis of IR spectral studies that alkyl 2-isothiocyanato and  $\omega$ -isothiocyanato carboxylates, in which the isothiocyanato and carboxyl groups are in  $\alpha$ -position to each other, exist in two conformations.

In the present study we summarise the studies of concentration dependence and solvent effects by infrared spectroscopy and the studies of dependence of chemical shifts on temperature in the compounds  $R^1R^2C(NCS)COOR^3$  where: *I*  $R^1, R^2 = H, R^3 = CH_3$ ; *II*  $R^1, R^2 = H; R^3 = C_2H_5$ ; *III*  $R^1, R^2 = H; R^3 = i-C_3H_7$ ; *IV*  $R^1 = H, R^2 = CH_3, R^3 = C_2H_5$ ; *V*  $R^1 = H, R^2, R^3 = C_2H_5$ ; *VI*  $R^1 = H, R^2 = i-C_3H_7, R^3 = C_2H_5$ ; *VII*  $R^1, R^2 = CH_3, R^3 = C_2H_5$ ; and compounds  $SCN \cdot (CH_2)_xCOOR$ , where X and R are: *VIII* X = 2, R =  $CH_3$ ; *IX* X = 2, R =  $C_2H_5$ ; X x = 3, R =  $C_2H_5$ ; *XI* x = 5, R =  $C_2H_5$ . We investigated the effect of solvents on the  $\nu(C=O)$  and  $\nu_{as}(NCS)$  bands in the IR spectra of seven esters of isothiocyanato carboxylic acids *II, IV-VI, IX-XI*.

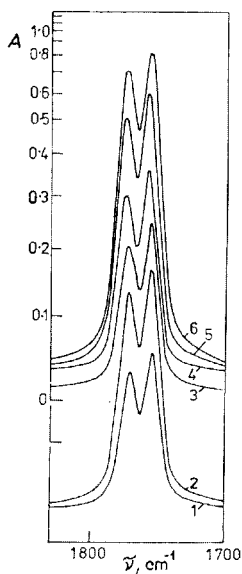


FIG. 1

Plot of Absorbance of the  $\nu(C=O)$  Band in the Spectrum of Ethyl Isothiocyanatoacetate against Concentration

$\nu(C=O)$  1772, 1751  $cm^{-1}$ ,  $\Delta\nu_{1/2}$  33 to 34  $cm^{-1}$ ;  $c$  [mm]: 1 0.782, 2 1.033, 3 1.825, 4 2.514, 5 14.946, 6 28.861; cell thickness: 1—4 0.9983 cm, 5, 6 0.0494 cm.

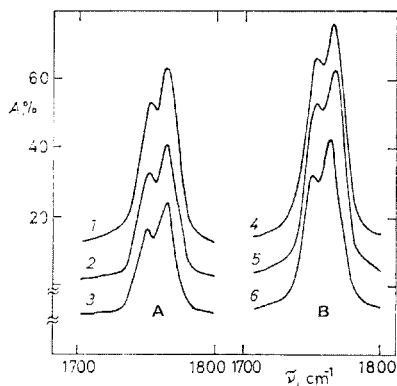


FIG. 2

Infrared Spectrum of Ethyl Isothiocyanatoacetate in Tetrahydrofuran (in the Region 1700—1800  $cm^{-1}$ )

$A$  ( $l = 0.006$  cm),  $c \cdot 10^{-2}$  [M]: 1 2.5, 2 1.66, 3 1.33;  $B$  ( $c = 0.25$  M),  $l \cdot 10^{-3}$  [cm]: 4 9.0, 5 8.0, 6 6.0.

In the studied isothiocyanates an intermolecular and intramolecular interaction can be considered. We can distinguish between them on the basis of the known effect of the concentration or the nature of solvent on the particular type of interaction. It is known that an intramolecular interaction is independent of concentration in a given solvent but it depends on solvent polarity.

The concentration dependence of the absorbance of the  $\nu(\text{C}=\text{O})$  band in *I* indicates an intramolecular interaction (Fig. 1). The  $\alpha$ -values are the same in all the measured cases ( $\alpha = \varepsilon_1^a/\varepsilon_2^a$ , where  $\varepsilon_1^a$  is the molar absorption coefficient of the  $\nu(\text{C}=\text{O})$  band at higher wavenumber). In order to evaluate the nature of the intramolecular interaction we measured spectra of the compounds *II*, *IV–VII* in various solvents and compared them with the spectra of *IX–XI*. The measurements in tetrahydrofuran were carried out at ten times higher concentration and in ten times thinner cells than in the case of the two other solvents. We studied therefore the concentration dependence and proved that comparison of such measurements is possible (Fig. 2).

It is seen from Table I that in chloroform the  $\nu(\text{C}=\text{O})$  band is shifted to lower wavenumbers. The bands in the spectra of the studied compounds are no longer splitted, the  $\varepsilon^a$  values are generally lower but the half-band widths are significantly greater than the half-band widths observed in  $\text{CCl}_4$ .

For the compounds *II*, *V* and *VI* the ratio  $\varepsilon_1^a/\varepsilon_2^a$  found in  $\text{CCl}_4$  is smaller than 1 whereas in chloroform it is greater than 1. This shows that in the latter solvent the amount of the conformer *A* increases whereas the amount of the conformer *B* decreases (Fig. 3). As seen from Fig. 4, the  $\nu(\text{C}=\text{O})$  bands in the spectrum of the compound *II* are poorly resolved; therefore in this case the population of the conformers can be only roughly estimated. No splitting was found in the spectra of other compounds of this series (*IV–VI*) taken in chloroform. Spectra of the compounds *IX–XI* (Table I) exhibit symmetric and unsplit  $\nu(\text{C}=\text{O})$  bands which thus allow a much simpler evaluation of the solvent effect. The effect of chloroform

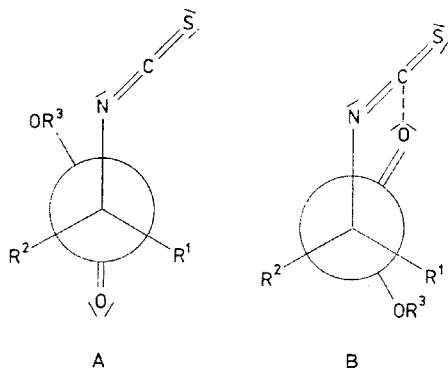


FIG. 3  
Newmann Projection of Conformers of Alkyl  
2-Isouthiocyanatocarboxylates

TABLE I  
Effect of Solvents on  $\nu(\text{C}=\text{O})$  Bands in the Spectra of Ethyl 2-Isothiocyanato- and  $\omega$ -Isothiocyanatocarboxylates

Compound	$\text{CCl}_4^a$			$\text{CHCl}_3^a$			Tetrahydrofuran <sup>a</sup>		
	$\tilde{\nu}_1$	$\epsilon_1^a$	$\Delta\nu_{1/2}$	$\tilde{\nu}_1$	$\epsilon_1^a$	$\Delta\nu_{1/2}$	$\tilde{\nu}_2$	$\epsilon_2^a$	$\Delta\nu_{1/2}$
II	1 768	288	31	1 753 <sup>b</sup>	304	39	1 764	281	30
IV	1 761 <sup>sh</sup>	—	28	1 753	332	36	(1 760) <sup>sh</sup>	—	29
V	1 761	284	26	1 741	304	36	1 757	299	27
VI	1 758	241	29	1 742	304	39	1 757	289	28
VII	—	—	20	—	—	—	(1 770) <sup>sh</sup>	—	21
IX	—	—	20	1 733	397	33	—	—	20
X	—	—	21	1 726	423	32	—	—	20
XI	—	—	24	1 724	397	34	—	—	19

<sup>a</sup> The values of  $\tilde{\nu}$  and  $\Delta\nu_{1/2}$  are given in  $\text{cm}^{-1}$ ,  $\epsilon^a$  in  $1 \text{ mol}^{-1} \text{ cm}^{-1}$ , the values in parentheses are approximate, sh shoulder; <sup>b</sup> further band  $\tilde{\nu}_2(\text{C}=\text{O})$  at  $1747 \text{ cm}^{-1}$ ,  $\epsilon_2^a = 279$ .

in the compound *XI* follows unequivocally from the lower wavenumber and greater half-width of the carbonyl band (Fig. 5).

All the  $\nu(\text{C}=\text{O})$  bands of the compounds *II*, *IV*, *V-VII* in tetrahydrofuran are splitted and the ratio of molar absorption coefficients of the two bands is reverse to that found in tetrachloromethane (Table I). The half-widths of the bands are within the range of values found in tetrachloromethane but they are smaller than in chloroform. The splitting, the difference between the wavenumbers of the doublet, and also the  $\varepsilon_1^a/\varepsilon_2^a$  ratio, indicate that in tetrahydrofuran the conformation *B* is markedly suppressed. The effect of the solvents on the  $\nu_{\text{as}}(\text{NCS})$  bands is seen from the data in Table II and from Figs 4 and 5. The main isothiocyanate bands in chloroform are generally situated at higher wavenumbers than in tetrachloromethane. This is in accord with our previous investigations, however, the changes

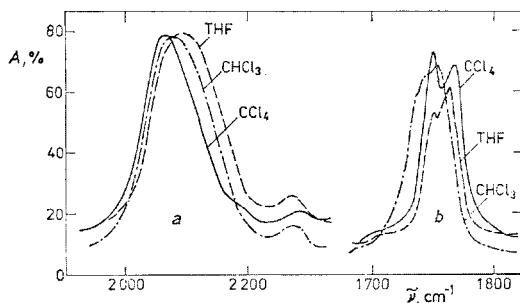


FIG. 4

Effect of Solvents on  $\nu(\text{C}=\text{O})$  and  $\nu_{\text{as}}(\text{NCS})$  Bands in the Spectrum of Ethyl Isothiocyanatoacetate  
*a*  $c = 0.02\text{M}$  ( $\text{CCl}_4$  and  $\text{CHCl}_3$ ),  $l = 0.08$  cm; *b*  $c = 0.25\text{M}$  (tetrahydrofuran),  $l = 0.006$  cm.

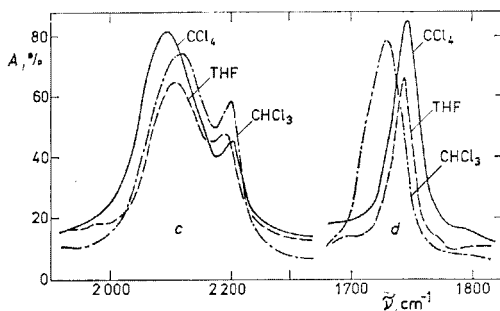


FIG. 5

Effect of Solvent on  $\nu(\text{C}=\text{O})$  and  $\nu_{\text{as}}(\text{NCS})$  Bands in the Spectrum of Ethyl 6-Isothiocyanatohexanoate

*c*  $c = 0.2\text{M}$  ( $\text{CCl}_4$  and  $\text{CHCl}_3$ ),  $l = 0.08$  cm; *c*  $c = 0.0842\text{M}$  (tetrahydrofuran),  $l = 0.01$  cm;  
*d*  $c = 0.02\text{M}$  ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ),  $l = 0.08$  cm; *c*  $c = 0.0842\text{M}$  (tetrahydrofuran),  $l = 0.008$ .

TABLE II  
Effect of Solvents on  $\nu_{as}(\text{NCS})$  Bands in the Spectra of Ethyl 2-Isothiocyanato- and  $\omega$ -Isothiocyanatocarboxylates

Compound	$\text{CCl}_4^a$					$\text{CHCl}_3^a$					Tetrahydrofuran <sup>a</sup>				
	$\tilde{\nu}_1$	$\epsilon_1^a$	$\tilde{\nu}_2$	$\epsilon_2^a$	$\Delta\nu_{1/2}$	$\tilde{\nu}_1$	$\epsilon_1^a$	$\tilde{\nu}_2$	$\epsilon_2^a$	$\Delta\nu_{1/2}$	$\tilde{\nu}_1$	$\epsilon_1^a$	$\tilde{\nu}_2$	$\epsilon_2^a$	$\Delta\nu_{1/2}$
II	—	—	2 065	507	108	—	—	2 072 <sup>b</sup>	407	130	—	—	2 092 <sup>c</sup>	374	125
IV	2 122	190	2 062	499	130	2 126	229	2 070	407	130	2 116	110	2 072	376	135
V	2 165 <sup>sh</sup>	94	2 064	565	130	2 156	122	2 073 <sup>d</sup>	407	137	2 165	114	2 075 <sup>e</sup>	382	113
VI	2 174 <sup>sh</sup>	50	2 070	487	115	2 132	239	2 076	420	135	2 144	219	2 085	400	120
VII	—	—	2 085 <sup>f</sup>	450	100	—	—	—	—	—	—	—	2 081 <sup>g</sup>	433	102
IX	2 160 <sup>sh</sup>	76	2 083	478	95	2 208	167	2 108	394	123	2 202	128	2 105	331	119
X	—	—	2 100	433	95	2 195	194	2 114	407	160	2 190	78	2 108	301	90
XI	—	—	2 093	413	100	2 197	219	2 113	320	160	2 192	139	2 105	227	150

<sup>a</sup> See footnotes in Table I; <sup>b</sup> further band at 2273  $\text{cm}^{-1}$  ( $\epsilon^a = 83$ ); <sup>c</sup> further band at 2274  $\text{cm}^{-1}$  ( $\epsilon^a = 50$ ); <sup>d</sup> further band at 2214  $\text{cm}^{-1}$  ( $\epsilon^a = 77$ ); <sup>e</sup> further band at 2214  $\text{cm}^{-1}$ ; <sup>f</sup> further band at 2031  $\text{cm}^{-1}$  ( $\epsilon^a = 384$ ,  $\Delta\nu_{1/2} = 60 \text{ cm}^{-1}$ ); <sup>g</sup> further band at 2032  $\text{cm}^{-1}$  ( $\epsilon^a = 293$ ,  $\Delta\nu_{1/2} = 72 \text{ cm}^{-1}$ ).

TABLE III

<sup>1</sup>H-NMR Spectra of Alkyl 2-Isothiocyanato- and ω-Isothiocyanatocarboxylates at 30° ± 0.5°C

Compound		
<i>I</i>		3.765, s, (CH <sub>3</sub> O)
<i>II</i>	1.285, t, (CH <sub>3</sub> ),	4.213, q, (CH <sub>2</sub> ),
<i>III</i>	1.228, d, (CH <sub>3</sub> ),	5.031, sep, (CH),
<i>IV</i>	1.231, t, (CH <sub>3</sub> ),	4.172, q, (CH <sub>2</sub> ),
<i>VII</i>	1.252, t, (CH <sub>3</sub> ),	4.168, q, (CH <sub>2</sub> ),
<i>VIII</i>	2.624, t,	3.750, t, (CH <sub>2</sub> —CH <sub>2</sub> ),

in the wavenumber of the second band are not regular (Table II). The  $\epsilon^a$  values are lower and the half-band widths significantly greater. The wavenumbers of  $\nu_{as}(\text{NCS})$  bands in compounds *II*, *IV*–*VI* are much higher, and their changes in going from  $\text{CCl}_4$  to  $\text{CHCl}_3$  (Table II) much greater, than those in compounds *IX*–*XI* where we did not observe any intramolecular interaction. The wavenumber of the main isothiocyanate band changes within the range observed for alkyl isothiocyanates,

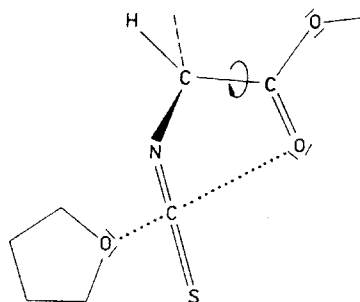


FIG. 6

Interaction of Alkyl 2-Isothiocyanatocarboxylates with Tetrahydrofuran (Dreiding Models).

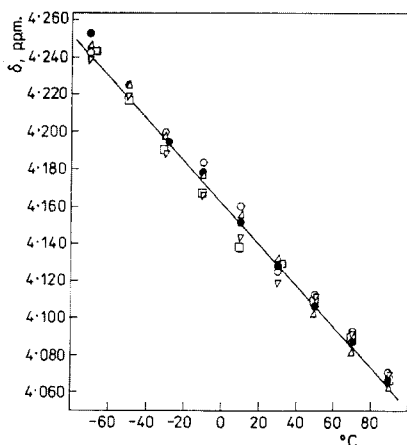


FIG. 7

Dependence of Chemical Shifts of Methylene Protons in Ethyl Isothiocyanatoacetate on Temperature and Concentration

Concentration (mg/ml):  $\nabla$   $c = 14.6$ ,  $\square$   $c = 23.4$ ,  $\circ$   $c = 29.6$ ,  $\triangle$   $c = 36.23$ ,  $\bullet$   $c = 51.0$ .

TABLE III  
(Continued)

$\delta$ [p.p.m.]	
	4.175, s, (CH <sub>2</sub> )
$J_{\text{CH}_3, \text{CH}_2} = 7.0$ ;	4.125, s, (CH <sub>2</sub> )
$J_{\text{CH}_3, \text{CH}} = 6.1$ ;	4.111, s, (CH <sub>2</sub> )
$J_{\text{CH}_3, \text{CH}_2} = 7.0$ ;	1.522, d, (CH <sub>3</sub> ), 4.247, q, (CH), $J_{\text{CH}, \text{CH}_3} = 6.7$
$J_{\text{CH}_3, \text{CH}_2} = 7.1$ ;	1.537, s, (CH <sub>3</sub> )
$J_{\text{CH}_2, \text{CH}_2} = 6.4$ ;	3.368, s, (CH <sub>3</sub> O)

the wavenumbers of other bands change in the opposite direction to the change of the main band; this is also in accord with the literature data<sup>9</sup>.

In tetrahydrofuran the wavenumbers of the main isothiocyanate band are in all cases higher than in chloroform. On the basis of electron density considerations we can expect that the isothiocyanate group can interact with chloroform at the sulphur and nitrogen atoms, whereas tetrahydrofuran interacts mainly with the carbon atom of the NCS group. From the marked increase of  $\nu_{\text{as}}(\text{NCS})$  we can conclude that the intramolecular interaction is affected by the solvation of the isothiocyanate group which lowers the electron density on the carbon. Thus, in tetrahydrofuran solution the intramolecular interaction is weaker, allowing a more facile rotation around the  $\sigma$  bonds of the "bridge" methylene or methine group(s) separating the ester and isothiocyanate groups. Therefore there is no reason for preferring the conformer *B* (Fig. 6).

The chemical shifts and coupling constants of the proton signals in the substituents R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, as well as of the protons in the —CH<sub>2</sub>— or —CH(R)— groups separating the isothiocyanate and ester groups, confirmed the structure and purity of the studied compounds *I–IV*, *VII–VIII* (Table III). As a result of the presence of two electron accepting substituents the chemical shifts of the methylene and methine protons are higher than the shifts of the protons next to the isothiocyanate group in alkyl isothiocyanates<sup>16</sup>. The chemical shifts in Table IV can be best compared to the analogous values of chemical shifts in ethyl chloroacetate<sup>17</sup>.

Chemical shifts in the spectra of the compound *II* were measured at five different concentrations (Fig. 7). In the region 14.60–50.98 mg/ml the effect of concentration on the chemical shift of the "bridge" methylene groups was 5% of the temperature effect. The chemical shift of the "bridge" methylene and methine groups depends linearly on temperature and the relationship  $\delta = k \cdot \tau + \delta_0$  has a great



correlation coefficient (Table IV). The chemical shift increases with decreasing temperature: this indicates a decrease in electron density in this group. On the basis of the solvent effects observed for the  $\nu(\text{C}=\text{O})$  and  $\nu_{\text{as}}(\text{NCS})$  bands in this study, as well as on the basis of our previous results, we proved the existence of two conformations, *A* and *B*, of which the amount of *B* increases with decreasing temperature.

As a result of a synperiplanar arrangement of the isothiocyanate and ester groups (Fig. 3) the donor-acceptor interaction between carbonyl and the carbon in the NCS group is stronger at lower temperatures; this manifests itself by smaller shielding of the methylene and methine groups in the "bridge" between the two functional groups. When the interacting groups are in a synperiplanar arrangement, the protons in question are in an antiperiplanar conformation relative to the carbonyl group. It is known<sup>18</sup> that the greatest transmission of electronic effects is in this arrangement.

With increasing temperature the mentioned donor-acceptor interaction is weaker and the antiperiplanar conformation of the isothiocyanate and carbalkoxyl groups is more preferred; this increases the charge density of the protons of the "bridge" between the groups and results in their smaller chemical shift. The dependence of the chemical shift of the substituents  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  on temperature was also linear and the results of the correlations are summarised in Table V. A comparison of the slopes (Table IV and V) shows no substantial effect of the temperature on the chemical

TABLE IV

Chemical Shift,  $\delta$  (p.p.m.), of the "Bridge" Methylene and Methine Groups in Alkyl 2-Isothiocyanatocarboxylates, and Its Dependence on Temperature

$T, ^\circ\text{C}$	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>VII</i> <sup>a</sup>
+70	4.128	4.082	4.068	4.213	1.362
+50	4.151	4.103	4.092	4.228	1.437
+30	4.171	4.131	4.111	4.247	—
+10	4.196	4.155	4.131	4.268	1.610
-10	4.221	4.176	4.152	4.285	1.676
-30	4.246	4.198	4.177	4.306	1.762
-50	4.268	4.225	4.201	4.335	1.871
-70	4.290	4.246	4.221	4.355	1.982
$r^b$	0.999	0.999	0.999	0.997	0.997
$k \cdot 10^{3c}$	-1.17	-1.18	-1.09	-1.03	-4.3
$\delta_0^d$	4.209	4.164	4.144	4.279	1.654

<sup>a</sup> Methyl signals; <sup>b</sup> correlation coefficient; <sup>c</sup> slope of the relationship  $\delta = k \cdot T + \delta_0$ , (p.p.m./ $^\circ\text{C}$ ); <sup>d</sup>  $\delta_0$  p.p.m.).

shifts of the substituents  $R^1$ ,  $R^2$  and  $R^3$ . The relatively high value of the slope found for the substituent  $R^2$  in the compound *IV* is connected with its direct bonding to the "bridge" methylene group. The temperature dependence studies revealed a weak signal in the spectrum of the compound *VII* which coalesced at 30°C with the signal of the substituents  $R^1$  and  $R^2$  and which also was linearly dependent on temperature (Table IV). Although it is obvious that this signal is related to the conformations of this compound, the present data cannot elucidate its origin.

### EXPERIMENTAL

The isothiocyanates, used in the measurements, are already known compounds<sup>1</sup>. The new derivative *VII* was synthesized following the procedure *A* in ref.<sup>1</sup>. For  $C_7H_{11}NO_2S$  (173.2) calculated: 8.08% N, 18.51% S; found: 8.29% N, 18.70% S. All the compounds were distilled before measurements. The infrared spectra were taken on a Unicam SP 100 G instrument in NaCl cells in various solvents. Spectral grade  $CCl_4$  and tetrahydrofuran were used without further purification. Chloroform (analytical grade) was passed repeatedly through a silica gel column in order to remove water and ethanol. The wavenumber scale was calibrated by a polystyrene foil, accuracy  $\pm 0.5 \text{ cm}^{-1}$  for the carbonyl region and  $\pm 1 \text{ cm}^{-1}$  for the region 2000–2200  $\text{cm}^{-1}$ . The  $\epsilon^a$  values were determined using the base-line method.<sup>1</sup>  $^1\text{H-NMR}$  spectra were measured in deuteriochloroform (Isocomerz, Berlin, 99.6% isotopic purity) on a Tesla BS-487 B instrument (80 MHz), using hexamethyldisiloxane as internal standard. The positions of the signals were determined

TABLE V

Temperature Dependence of the Chemical Shift of the Substituents  $R^1$ ,  $R^2$  and  $R^3$  in Compounds  $R^1R^2C(NCS)COOR^3$

Compound	R	$r^a$	$k \cdot 10^3$ p.p.m./°C	$\delta_0$ , p.p.m.	
<i>I</i>	$R^3$	CH <sub>3</sub>	0.996	-0.3	3.767
		CH <sub>3</sub>			—
<i>II</i>	$R^3$	CH <sub>2</sub>	0.976	0.1	4.27
		CH <sub>3</sub>	0.934	-0.03	1.232
<i>III</i>	$R^3$	CH	0.900	-0.26	5.056
		CH <sub>3</sub>	0.991	-0.1	1.253
<i>IV</i>	$R^3$	CH <sub>2</sub>	0.910	-0.04	4.177
		CH <sub>3</sub>	0.996	-0.5	1.534
	$R^2$	CH <sub>3</sub>	0.996	-0.2	1.258
<i>VII</i>	$R^3$	CH <sub>2</sub>	0.970	-0.16	4.172
	$R^1, R^2$	CH <sub>3</sub>	0.997	-0.36	1.546

<sup>a</sup> Twelve experimental points were used in the correlation.

with an accuracy  $\pm 0.2$  Hz. The compounds were measured in the temperature interval  $+70^{\circ}\text{C}$  to  $-70^{\circ}\text{C}$  (accuracy of the temperature data  $\pm 0.5^{\circ}\text{C}$ ). The chemical shifts were correlated with temperature using a Hewlett Packard 9810 A computer.

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