

Isothiocyanates and Their Synthetic Producers. IX. Synthesis and Study of the Infrared, Ultraviolet, and NMR Spectra of 4'-Substituted 3-Isothiocyanato- and 4-Isothiocyanatochalcones

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In this paper the synthesis of 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones *via* nitro- and aminochalcones is described. The infrared, ultraviolet, and NMR spectra of above compounds are studied. It follows from the study of infrared spectra that the rotational isomers exist only in the presence of electron-acceptor substituents in the 4'-position.

Several papers [1—4] were devoted to the preparation of chalcones and the study of their infrared and ultraviolet absorption spectra. *Cukerman* and co-workers [5] studied the effect of substituents on the position of the absorption bands corresponding to the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ vibrations as well as the existence of *s-cis* and *s-trans* isomers of these compounds in solution. In our preceding paper [6] we concerned with the study of the infrared and ultraviolet absorption spectra of 4-substituted 3'-isothiocyanato- and 4'-isothiocyanatochalcones and we found that the formation of rotational isomers might take place only in the presence of electron-donor substituents.

For this reason, we aimed at preparing a series of 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones and studying their infrared, ultraviolet, and NMR spectra as well.

The 4'-substituted 3-nitro- and 4-nitrochalcones as well as the 4'-substituted 3-amino- and 4-aminochalcones were intermediates in the synthesis of isothiocyanates.

The 4'-substituted 3-nitro- and 4-nitrochalcones were prepared by aldol condensation of the relevant 4-substituted acetophenones with 3-nitro- and 4-nitrobenzaldehyde in ethanol under catalytic effect of 10% sodium hydroxide solution according to *Pratt* and co-workers [7].

The 4'-substituted 3-amino- and 4-aminochalcones were prepared by reduction of the corresponding substituted nitrochalcones with tin(II) chloride in glacial acetic acid and concentrated hydrochloric acid [8]. It was the thiophosgene method which was used for the preparation of isothiocyanates [9].

Experimental

Preparation of the 4'-substituted 3-nitro- and 4-nitrochalcones

3-Nitro- or 4-nitrobenzaldehyde (0.005 mole) and the 4-substituted acetophenone (0.005 mole) are dissolved in 120 ml of ethanol. 0.005 mole of 10% sodium hydroxide is dropwise added to the reaction mixture from a separatory funnel under intensive stirring;

in the course of one hour. Thereafter the reaction mixture has been stirred for another two hours and subsequently kept standing for 24 hours at room temperature. The separated 4'-substituted nitrochalcone is sucked, dried and recrystallized from a suitable solvent.

3-Nitrochalcone m.p. 145–146°C [10], 4'-methoxy-3-nitrochalcone (m.p. 152–155°C) [10], 4'-chloro-3-nitrochalcone (m.p. 150°C) [10], 4'-bromo-3-nitrochalcone (m.p. 158°C) [10], 4'-nitro-3-nitrochalcone (m.p. 206–208°C) [10], 4-nitrochalcone (m.p. 163°C) [11], 4'-methoxy-4-nitrochalcone (m.p. 157°C) [12], 4'-fluoro-4-nitrochalcone (m.p. 166°C) [13], 4'-chloro-4-nitrochalcone (m.p. 172°C) [10], 4'-bromo-4-nitrochalcone (m.p. 166°C) [14], 4'-methyl-4-nitrochalcone (m.p. 161°C) [15] were described previously.

4'-Methyl-3-nitrochalcone, m.p. 132–134°C, yield 90.04%.

For $C_{16}H_{13}NO_3$ (267.29) calculated: 71.36% C, 4.86% H; found: 71.25% C, 4.83% H.

4'-Cyano-4-nitrochalcone, m.p. 229–230°C, yield 92.10%.

For $C_{16}H_{10}N_2O_3$ (278.27) calculated: 69.05% C, 3.62% H; found: 69.07% C, 3.83% H.

4'-Cyano-3-nitrochalcone, m.p. 224–225°C, yield 83.20%.

For $C_{16}H_{10}N_2O_3$ (278.27) calculated: 69.05% C, 3.62% H; found: 68.96% C, 3.58% H.

Preparation of the 4'-substituted 3-amino- and 4-aminochalcones

Tin(II) chloride (0.02 mole) is dissolved in 10 ml of hydrochloric acid and 3 ml of glacial acetic acid. During 30 minutes 4'-substituted nitrochalcone (0.005 mole) is added in parts into the reduction agent while stirring at 30–35°C. The temperature of reaction mixture rises to 75–80°C and the stirring continues for another two hours. The complex compound formed is sucked, dissolved in 100 ml of distilled water, and neutralized with ammonia. A precipitate which has been formed during this operation is sucked and dried. Afterwards it is extracted by acetone in Soxhlet apparatus. After evaporating acetone, crude aminochalcone is recrystallized from a convenient solvent.

The data characterizing the synthesized aminochalcones are presented in Table 1.

Preparation of the 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones

The 4'-substituted aminochalcone (0.01 mole) is dissolved in 100 ml of chloroform and this solution is successively added during 30 minutes under stirring into a mixture of thiophosgene (0.011 mole), calcium carbonate (0.011 mole), water (150 ml), and chloroform (100 ml). Stirring of the reaction mixture continues for another two hours. The chloroform layer is separated and dried with anhydrous calcium chloride and then chloroform is removed by vacuum distillation. The crude product is twice recrystallized from a suitable solvent containing active charcoal.

The data characterizing the synthesized isothiocyanate are presented in Table 2.

Spectral measurements

The infrared absorption spectra of isothiocyanatochalcones were measured by means of the double-beam spectrophotometer UR-20 (Zeiss, Jena) in the region of 800–3500 cm^{-1} . The measurements were performed with chloroform solutions containing the substances in the concentration of 0.02 mole l^{-1} by using the cell lengths of 0.4 mm. The spectra of substituted isothiocyanate occurring in the region between 1500 and 1800 cm^{-1} are presented in Table 3. They were measured in carbon tetrachloride (concentration 0.02 mole l^{-1} , cell length 0.4 mm) and in KBr discs (2 mg of substance, 1.1 g of KBr). The instrument was calibrated with respect to wave number by means of a polystyrene foil.

Table 1
 Survey of the synthesized 4'-X-3-amino- (*I*–*VII*) and 4'-X-4-aminochalcones
 (*VIII*–*XIV*)

No.	X	Molecular formula	<i>M</i>	Calculated/found		Yield [%]	M.p. [°C]	M.p. [°C]
				% C	% H			
<i>I</i>	H	C ₁₅ H ₁₃ NO	223.28			82.6	158–159 (toluene)	159 ref. [14]
<i>II</i>	CH ₃	C ₁₆ H ₁₅ NO	237.30	80.98 81.02	6.37 6.23	81.2	123–124.5 (toluene)	
<i>III</i>	CH ₃ O	C ₁₆ H ₁₅ NO ₂	253.30			82.1	141–142.5 (toluene)	144–145 ref. [11]
<i>IV</i>	Cl	C ₁₅ H ₁₂ ClNO	257.73	69.91 69.85	4.69 4.54	82.8	120–121.5 (toluene)	
<i>V</i>	Br	C ₁₅ H ₁₂ BrNO	302.19	59.61 59.32	4.01 3.98	83.9	149–151 (toluene)	
<i>VI</i>	NH ₂	C ₁₅ H ₁₄ N ₂ O	183.29	75.60 75.82	5.92 5.65	82.9	167–169 (chlorobenzene)	
<i>VII</i>	CN	C ₁₆ H ₁₂ N ₂ O	248.29	77.39 77.40	4.87 4.62	83.1	130–131 (acetone)	
<i>VIII</i>	H	C ₁₅ H ₁₃ NO	223.28			73.4	154.5–156 (acetone)	151–152 ref. [13]
<i>IX</i>	CH ₃ O	C ₁₆ H ₁₅ NO ₂	253.30			70.9	179–181 (toluene)	173–174 ref. [24]
<i>X</i>	F	C ₁₅ H ₁₂ FNO	241.27	75.13 74.98	5.03 5.14	81.2	134.5–136 (toluene)	
<i>XI</i>	Cl	C ₁₅ H ₁₂ ClNO	257.73	69.91 69.76	4.69 4.84	88.1	130.5–132 (toluene)	
<i>XII</i>	Br	C ₁₅ H ₁₂ BrNO	302.19			85.9	155–156 (toluene)	154 ref. [10]
<i>XIII</i>	CH ₃	C ₁₆ H ₁₅ NO	237.30	80.98 80.73	6.37 6.39	69.8	130–132 (toluene)	
<i>XIV</i>	CN	C ₁₆ H ₁₂ N ₂ O	248.29	77.39 77.46	4.87 4.98	73.4	180–183 (acetone)	

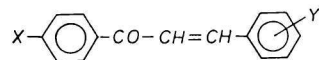
Table 2

Survey of the synthesized 4'-X-3-isothiocyanato- (I–VII) and 4'-X-4-isothiocyanato-chalcones (VIII–XIV)

No.	X	Molecular formula	M	Calculated/found		Yield [%]	M.p. [°C]
				% N	% S		
I	H	C ₁₆ H ₁₁ NOS	265.34	5.27	12.08	72.4	86.5–87
				5.24	12.08		(<i>n</i> -heptane)
II	CH ₃	C ₁₇ H ₁₃ NOS	279.37	5.01	11.47	87.8	97–97.5
				4.97	11.42		(<i>n</i> -heptane)
III	CH ₃ O	C ₁₇ H ₁₃ NO ₂ S	295.37	4.74	10.85	71.1	125.5–126.5
				4.82	10.87		(<i>n</i> -heptane)
IV	Cl	C ₁₆ H ₁₀ ClNOS	299.79	4.67	10.69	78.5	143–144
				4.77	10.89		(acetone)
V	Br	C ₁₆ H ₁₀ BrNOS	344.25	4.07	9.31	82.8	142–143.5
				3.89	9.37		(acetone)
VI	NCS	C ₁₇ H ₁₀ N ₂ OS ₂	332.42	8.68	19.86	71.4	154–154.5
				8.70	19.67		(acetone)
VII	CN	C ₁₇ H ₁₀ N ₂ OS	290.35	9.65	11.04	77.5	183–184.5
				9.37	10.85		(acetone)
VIII	H	C ₁₆ H ₁₁ NOS	265.34	5.27	12.08	68.4	130.5–132
				5.25	12.13		(<i>n</i> -heptane)
IX	CH ₃ O	C ₁₇ H ₁₃ NO ₂ S	295.37	4.74	10.85	72.3	149.5–151
				4.58	10.74		(carbon tetrachloride)
X	F	C ₁₆ H ₁₀ FNOS	283.33	4.94	11.32	67.3	135–136.5
				4.83	11.49		(<i>n</i> -heptane)
XI	Cl	C ₁₆ H ₁₀ ClNOS	299.79	4.67	10.69	69.6	146–148
				4.88	10.52		(<i>n</i> -heptane)
XII	Br	C ₁₆ H ₁₀ BrNOS	344.25	4.07	9.31	72.6	147–148
				4.06	9.11		(<i>n</i> -heptane)
XIII	CH ₃	C ₁₇ H ₁₃ NOS	279.37	5.01	11.47	73.4	148–149
				4.95	11.50		(<i>n</i> -heptane)
XIV	CN	C ₁₇ H ₁₀ N ₂ OS	290.35	9.65	11.04	62.6	183–184.5
				9.84	11.21		(acetone)

Table 3

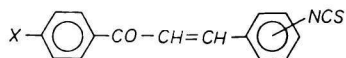
Characteristic frequencies in the infrared spectra of 4'-X-3-isothiocyanato- and 4'-X-4-isothiocyanatochalcones given in cm^{-1}



No.	X	Y	Chloroform		Carbon tetrachloride		KBr discs	
			$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$
I	H	H	1666	1609	1672	1613	1664	1608
			1641		1652			
II	H	3-NCS	1663	1611	1678	1616	1664	1612
			1646		1658			
III	H	4-NCS	1668	1602	1677	1613	1661	1601
			1642		1656			
IV	CH_3O	3-NCS	1667	1604	1672	1616	1668	1619
V	CH_3O	4-NCS	1662	1604	1672	1613	1658	1605
VI	CN	3-NCS	1676	1618	insoluble		1672	1617
			1655					
VII	CN	4-NCS	1672	1615	insoluble		1667	1616
			1650					

Table 4

Characteristic frequencies in the infrared spectra and absorption maxima in the ultraviolet spectra of 4'-X-3-isothiocyanato- (VIII–XIV) and 4'-X-4-isothiocyanatochalcones (I–VII) given in cm^{-1} and nm, respectively



No.	X	$\delta(\text{C-H})$ <i>trans</i>	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{NCS})$	$\nu(\text{CH arom.})$	λ_{max} log ϵ	λ_{max} log ϵ
I	CH ₃ O	984	1610	1662	2108	3038	225	336
II	CH ₃	983	1614	1668	2109	3041	4.40 225	4.67 334
III	H	984	1602	1688 1642	2109	3045	4.34 225	4.64 334
IV	F	985	1610	1669	2110	3041	4.31 225	4.60 332
V	Cl	984	1613	1608	2112	3043	4.33 225	4.63 334
VI	Br	984	1608	1668 1646	2110	3045	4.43 225	4.59 336
VII	CN	983	1615	1672 1656	2108	3042	4.36 233	4.65 342
VIII	CH ₃ O	984	1605	1664	2115	3045	4.24 280	4.59 314
IX	CH ₃	985	1606	1669	2111	3041	4.49 280	4.47 299
X	H	984	1608	1669 1646	2114	3044	4.54 280	4.51 295
XI	Cl	984	1608	1671 1649	2110	3047	4.54 280	4.46 300
XII	Br	985	1608	1668 1648	2109	3043	4.54 281	4.50 298
XIII	NCS	983	1603	1670	2110	3040	4.57 282	4.53 318
XIV	CN	983	1618	1676 1655	2110	3039	4.48 280	4.63 300
							4.50	4.43

The ultraviolet absorption spectra were measured by means of the spectrophotometer VSU-1 (Zeiss, Jena) in methanol (concentration 1.5×10^{-5} – 2.5×10^{-5} mole l⁻¹, cell length 10 mm) at $20 \pm 2^\circ\text{C}$. The absorbance in the regions of maxima was measured in intervals of 2 nm otherwise of 5 nm.

The NMR spectra of isothiocyanatochalcones were taken at 60 MHz in deuteriochloroform by means of the spectrophotometer Varian A-60 while tetramethylsilane was used as an internal standard.

Discussion

In this paper the preparation of fourteen new 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones as well as their intermediates (nitro- and amino-chalcones) is reported.

The infrared absorption spectra of substituted isothiocyanatochalcones exhibit a relatively intense absorption band in the region of 980 cm^{-1} which is characteristic for the disubstituted *trans*-olefins (deformation, non-planar vibrations of the C—H bonds [16]).

In the region from 1600 to 1700 cm^{-1} the infrared absorption spectra of chalcones show the absorption bands corresponding to stretching vibrations of the vinyl and carbonyl groups. *Bellami* [17] assigns three absorption bands 1608 , 1650 , and 1671 cm^{-1} to the vibrations of benzene ring, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ vibrations, respectively. *Cukerman* and co-workers [5] demonstrated on the basis of the study of the infrared absorption spectra of monosubstituted chalcones in chloroform, carbon tetrachloride and KBr discs that the absorption band at 1608 cm^{-1} belongs to the $\nu(\text{C}=\text{C})$ stretching vibrations while the absorption bands at 1650 and 1671 cm^{-1} correspond to the $\nu(\text{C}=\text{O})$ stretching vibrations either of the *s-trans*- or *s-cis*-form of chalcone, respectively. To identify the frequency of carbonyl groups, they used the procedure of *Bellami* [18] which consists in comparing the spectra of chalcones in chloroform with those taken in carbon tetrachloride. A sensible shift of the $\nu(\text{C}=\text{O})$ bond frequencies to lower values is to be observed in chloroform. The infrared absorption spectra of chalcones in KBr discs exhibited only two absorption bands in this region namely at 1610 and 1669 cm^{-1} and they ascribed them the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ vibration frequencies, respectively (absence of rotation isomers).

We have studied the rotation isomers by using some selected substituted isothiocyanatochalcones the characteristic frequencies of which are given for chloroform, carbon tetrachloride, and KBr discs in Table 3. The generation of rotational isomers of 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones is controlled by the —I effect of NCS group and the infrared absorption spectra exhibited a doubling of the absorption bands corresponding to carbonyl groups. The rotational isomers appeared in the case of the nonsubstituted chalcone as well as of the substituents with —M effect (Table 3, derivatives *I–III* and *VI, VII*). All above derivatives possessed two absorption maxima in the region of $\nu(\text{C}=\text{O})$ frequencies while the absorption maximum corresponding to the lower frequency had the character of a shoulder (Table 3, Fig. 1).

We have attributed the absorption band at 1645 cm^{-1} to the *trans*-form and the absorption band at 1670 cm^{-1} to the *cis*-form in agreement with the results of preceding authors. Provided that a methoxy group is put in the 4-position, the rotation isomerism disappears and the $\nu(\text{C}=\text{O})$ vibration frequencies exhibit a single absorption band at 1670 cm^{-1} (Table 3, derivatives *IV, V*, Fig. 1).

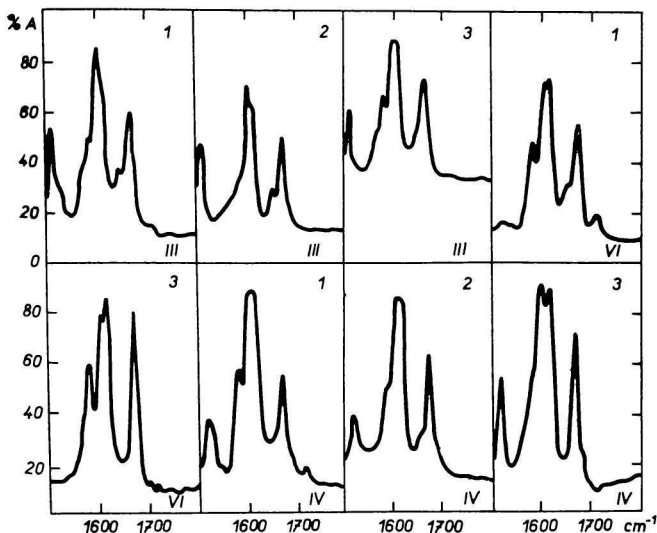


Fig. 1. Infrared absorption spectra of 4-isothiocyanatochalcone (III), 4'-cyano-3-isothiocyanatochalcone (VI), 4'-methoxy-3-isothiocyanatochalcone (IV).

1. in chloroform; 2. in carbon tetrachloride; 3. in KBr discs.

It follows from these facts that the electron-donor substituents reduce the conjugation of the styrene remainder with carbonyl group. This effect causes that the linkage between carbonyl and vinyl groups has the character of a simple bond with free rotation and the rotational isomers are not to be observed in infrared absorption spectra.

The substituents with $-I$ and $-M$ effects having electron-acceptor nature cause the increase in electron-defect on the carbonyl group what supports the conjugation effect with the second aromatic ring. For this reason, the rotational isomers are formed in this case.

In solid form (KBr discs), these derivatives exhibited only two maxima namely in the region between 1610 and 1670 cm^{-1} which belonged to the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ frequencies, respectively (Table 3, derivatives I–VII, Fig. 1).

The 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones exhibit some intense, broad absorption bands in the region from 2000 to 2200 cm^{-1} which correspond to $\nu_{\text{as}}(\text{NCS})$. The absorption maxima of these bands do not change practically by the effect of the substituents in the 4'-position of the neighbouring ring ($\nu_{\text{as}}(\text{NCS}) \sim 2110\text{ cm}^{-1}$) (Table 4).

The ultraviolet absorption spectra of the 4'-substituted 3-isothiocyanato- and 4-isothiocyanatochalcones are presented in Figs. 2 and 3 while the values of their absorption maxima and logarithms of extinction coefficients are given in Table 4. The ultraviolet absorption spectra of the substituted isothiocyanatochalcones were measured in methanol and in the spectral region from 220 to 400 nm .

There are two absorption maxima *i.e.* at 230 nm (band II) and at 310 nm (band I) which are usually characteristic for *trans*-chalcones [4]. At first, these maxima were attributed to particular chromophore systems in a molecule of chalcone (benzoyl,

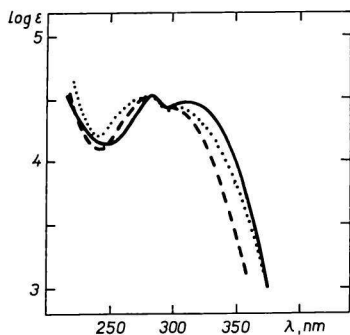


Fig. 2. Ultraviolet absorption spectra of isothiocyanatochalcones.

— 4'-methoxy-3-isothiocyanatochalcone;
 --- 3-isothiocyanatochalcone;
 . . . 4'-cyano-3-isothiocyanatochalcone.

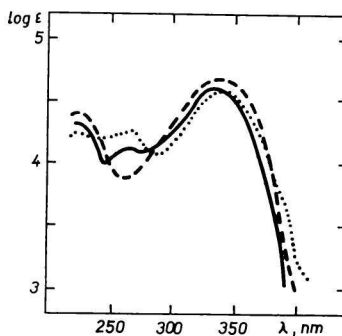


Fig. 3. Ultraviolet absorption spectra of isothiocyanatochalcones.

— 4-isothiocyanatochalcone;
 --- 4'-methoxy-4-isothiocyanatochalcone;
 . . . 4'-cyano-4-isothiocyanatochalcone.

cinnamoyl). Recently, the absorption band at higher wavelengths (band I, *K*-band) is attributed to the whole conjugated system [3, 4]. The third band at 205 nm in the spectra of chalcones belongs to the modified benzene ring [19, 20].

In the case of *cis*-chalcones as well as some *trans*-chalcones, so called „central band“ at 250 nm appears which is assumed to be likely the result of absorption of the benzoylvinyl remainder [21, 22].

By evaluating our results we have found that the „central band“ in the 250–280 nm region appears only in the case of the 4'-substituted 3-isothiocyanato-

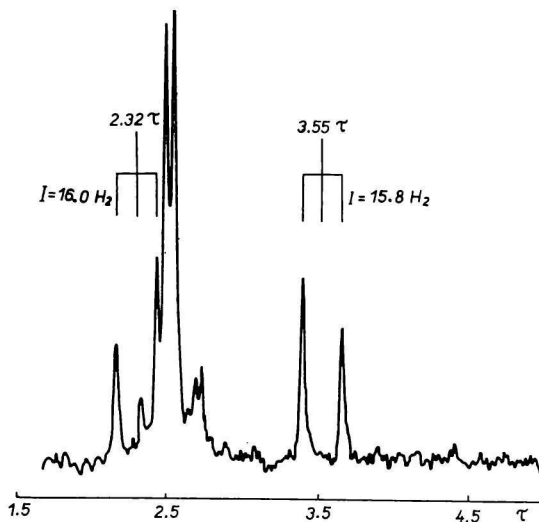


Fig. 4. NMR spectrum of 4-bromocinnamoylisothiocyanate measured at 60 MHz in deuteriochloroform with tetramethylsilane as an internal standard.

chalcones (Table 4, derivatives VIII—XIV) while it is absent in the case of 4'-substituted 4-isothiocyanatochalcones. Opposite to 3-isothiocyanatochalcone ($\lambda_{\max} = 295$ nm), 4-isothiocyanatochalcone ($\lambda_{\max} = 334$ nm) exhibits a bathochromic effect with respect to the nonsubstituted chalcone ($\lambda_{\max} = 310$ nm) indicating the $+M$ effect of the NCS group with the conjugated system of chalcone. This bathochromic effect is also to be observed with other 4'-substituted 4-isothiocyanatochalcones in contrast to the 4'-substituted 3-isothiocyanatochalcones.

To prove the existence of the rotational isomers assumed on the basis of infrared absorption spectra of these compounds we measured the NMR spectra of their fundamental representatives namely 3-isothiocyanatochalcone and 4-isothiocyanatochalcone. We did not succeed in identifying the rotational isomers because the resonance signals of both methine protons occur in the resonance region of aromatic protons.

In this connection, we have paid attention to the possibility of existence of the rotational isomers of other types of isothiocyanato- α,β -unsaturated ketones which were described in our foregoing paper [23]. From these compounds, we selected 4-bromocinnamoylisothiocyanate because of its stability and good solubility. The methine protons of this derivative give two doublets namely at about 3.55 and 2.32 τ with the constant of spin interaction of 15.8 and 16.0 Hz, respectively what indicates a *trans*-isomer (Fig. 4). The presence of rotational isomers has not been proved even at -40°C .

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