

Isothiocyanates. XXXVI. The synthesis of substituted 4-benzylthio-, 4-[(phenylthio)methyl]phenyl isothiocyanates, and the corresponding sulfones

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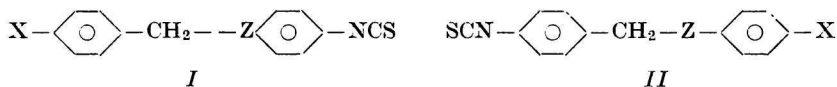
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The synthesis of 16 novel isothiocyanates, 12 intermediates, and their infrared and ultraviolet absorption spectra are described.

In our continuing project on isothiocyanates containing sulfur in addition to the mentioned functional group attention is being paid to the synthesis of a series of isothiocyanate of general formula



where X in formula I = H, CH₃, Br, CN, NO₂, and NCS; in formula II, X = H, CH₃, Cl, and Br; and Z for both formulas = S, SO₂.

Of this series only 4-benzylthiophenyl isothiocyanate prepared by dithiocarbamate procedure and patented as insecticide [1], 4-benzylsulfonylphenyl isothiocyanate obtained through thiophosgene and used as fungicide [2–4], and 4-[(4-chlorophenylthio)methyl]phenyl isothiocyanate exhibiting acaricide effect [5] were synthesized.

Experimental

Infrared spectra of isothiocyanates were measured on a double-beam UR-10 Zeiss spectrophotometer in the 800–3600 cm⁻¹ range in NaCl cells 0.500 mm in width; concentration 2.5×10^{-2} M in chloroform. The apparatus was calibrated with a polystyrene foil 25 μm thick. Ultraviolet absorption spectra were recorded on an ORD/UV-5 JASCO spectrophotometer in the 210–400 nm region in 1-cm cells; concentration $1.3\text{--}2.2 \times 10^{-5}$ M in ethanol at $22 \pm 2^\circ\text{C}$.

Starting materials

Benzyl chloride was a commercial product, 4-bromobenzyl chloride was prepared by chlorination of 4-bromotoluene in 50% yield [6]. 4-Nitrobenzyl bromide in 52.4%,

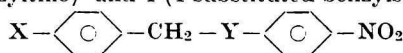
according to [7], 4-cyanobenzyl chloride from 4-tolunitrile in 54.5% [8], and 4-methylbenzyl chloride in 51.5% yield [9]. Sodium 4-nitrothiophenoxide was obtained from 4-nitrochlorobenzene and Na_2S_2 [10].

Thiophenol, *p*-toluene sulfochloride and sodium benzene sulfinate were commercially available, *p*-chlorobenzene sulfochloride was prepared by sulfochlorination of chlorobenzene according to [16] in 58% yield. *p*-Bromobenzene sulfochloride was obtained from *p*-bromoaniline [17] in 78% yield and *p*-acetamidobenzene sulfochloride by sulfochlorination of acetanilide [18]. *p*-Methylthiophenol was prepared by reduction of *p*-toluene sulfochloride with iron in glacial acetic acid [19] (52.3%). *p*-Chloro- and *p*-bromothiophenol were synthesized according to [12] in 71 and 63.5% yield, respectively. *p*-Acetamidothiophenol was prepared by reduction of *p*-acetamidobenzene sulfochloride with zinc in concentrated hydrochloric acid [20]. Sodium *p*-acetamidobenzene sulfinate was obtained from the corresponding sulfochloride with sodium sulfite [18].

The nitrosulfides *I*–*V* (Table 1) were prepared by condensation of 4-substituted benzyl halogenide with sodium *p*-nitrophenoxide [11]; nitrosulfides belonging to the series *II* were prepared by condensation of 4-nitrobenzyl halides with 4-substituted thiophenol in alcoholic medium in the presence of an alkali metal hydroxide [4, 5, 13]. Nitrosulfones *VI*–*X* and others were obtained by oxidation of the corresponding nitrosulfides with 30% hydrogen peroxide in glacial acetic acid [12] excepting [(phenylsulfonyl)methyl]nitrobenzene, which was synthesized by condensation of 4-nitrobenzyl bromide with sodium benzene sulfinate [21].

Table 1

4-(4-Substituted benzylthio)- and 4-(4-substituted benzylsulfonyl)nitrobenzenes

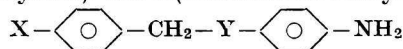


No.	X	Y	Formula	M	Calculated/found		Yield [%]	M.p. [°C]
					% N	% S		
<i>I</i>	H	S	$\text{C}_{13}\text{H}_{11}\text{NO}_2\text{S}$	245.30	—	—	71.5	122
<i>II</i>	CH_3	S	$\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$	259.32	5.40 5.45	12.36 12.80	61.6	87–90
<i>III</i>	Br	S	$\text{C}_{13}\text{H}_{10}\text{BrNO}_2\text{S}$	324.20	4.32 4.47	9.89 9.94	58.3	130
<i>IV</i>	CN	S	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$	270.30	10.36 10.13	11.81 11.73	71.2	151–153
<i>V</i>	NO_2	S	$\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4\text{S}$	290.30	—	—	83.2	107–109
<i>VI</i>	H	SO_2	$\text{C}_{14}\text{H}_{11}\text{NO}_4\text{S}$	277.30	—	—	71.5	169–171
<i>VII</i>	CH_3	SO_2	$\text{C}_{14}\text{H}_{13}\text{NO}_4\text{S}$	291.33	4.81 5.07	11.01 11.35	56.5	178–179
<i>VIII</i>	Br	SO_2	$\text{C}_{13}\text{H}_{10}\text{BrNO}_4\text{S}$	356.20	3.93 ^a 4.10	9.00 9.07	57.8	193
<i>IX</i>	CN	SO_2	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4\text{S}$	302.31	9.27 9.36	10.61 10.82	68.3	168
<i>X</i>	NO_2	SO_2	$\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_6\text{S}$	322.20	—	—	51.5	191

a) % Br calculated/found: 22.43
22.98

Table 2

4-(4-Substituted benzylthio)- and 4-(4-substituted benzylsulfonyl)anilines



No.	X	Y	Formula	<i>M</i>	Calculated/found		Yield [%]	M.p. [°C] B.p. [°C/torr]
					% N	% S		
XI	H	S	C ₁₃ H ₁₃ NS	215.2	—	—	57.6	202/8
XII	CH ₃	S	C ₁₄ H ₁₅ NS	229.5	6.30	13.9	56.0	75–78
XIII	Br	S	C ₁₃ H ₁₂ BrNS	294.2	5.97	14.23	50.0	109–110
					4.76	10.3		
XIV	CN	S	C ₁₄ H ₁₂ N ₂ S	240.3	4.89	11.05	88.0	138
					11.65	13.33		
XV	NO ₂	S	C ₁₃ H ₁₂ N ₂ O ₂ S	260.31	11.55	13.53	73.3	103–105
					—	—		
XVI	NH ₂	S	C ₁₃ H ₁₄ N ₂ S	230.33	—	—	65.5	99–101
					—	—		
XVII	H	SO ₂	C ₁₃ H ₁₃ NO ₂ S	247.32	—	—	63.4	219
					—	—		
XVIII	CH ₃	SO ₂	C ₁₄ H ₁₅ NO ₂ S	261.34	5.37	12.28	75.2	230–234
					5.57	12.07		
XIX	NO ₂	SO ₂	C ₁₄ H ₁₃ ClN ₂ O ₄ S	292.32	8.52 ^b	9.75	65.2	290–294 ^a
					8.68	9.72		
XX	NH ₂	SO ₂	C ₁₃ H ₁₄ N ₂ O ₂ S	262.33	—	—	65.7	214
					—	—		

a) Isolated as hydrochloride;

b) % Cl calculated/found: 10.80
10.70

Amino derivatives of the sulfide XI–XVI and sulfone XVII–XX series (Table 2) were synthesized by reduction of the corresponding nitro derivatives with tin in concentrated hydrochloric acid [13]. The 4-(4-nitrobenzylthio)aniline and 4-(4-nitrobenzylsulfonyl)aniline were prepared by condensation of 4-nitrobenzyl bromide with 4-acetamidothiophenol or sodium 4-acetamidobenzene sulfinate followed by a hydrolysis [14, 15]. [(Phenylthio)methyl]aniline was the product of condensation of thiophenol with formaldehyde and aniline in acid medium [22].

4-[(4-Chlorophenylsulfonyl)methyl]aniline (m.p. 207–209°C) obtained in 75% yield has not been described as yet.

For C₁₃H₁₂ClNO₂S (281.76) calculated: 4.97% N; 11.30% S; 12.15% Cl; found: 5.10% N; 11.23% S; 12.38% Cl.

4-(4-*X*-benzylthio)- (XXI–XXVI), 4-(4-*X*-benzylsulfonyl)- (XXVII–XXX),
4-[(4-*X*-phenylthio)methyl]- (XXXI–XXXIV),
and 4-[(4-*X*-phenylsulfonyl)methyl]phenyl isothiocyanates (XXXV–XXXVIII)

Thiophosgene (0.055 mole), chloroform (25 ml) and water (50 ml) were placed into a two-necked flask equipped with an efficient stirrer and a dropping funnel. The vigorously stirred content of the flask formed an emulsion to which a solution of the appro-

prate amine (0.05 mole) in chloroform (50 ml) was added during 1/2 hour. To neutralize the acid formed NaHCO_3 or CaCO_3 was poured into the mixture. After the amine had completely been added, the reaction mixture was stirred for 1/2 to 1 hour, the organic layer was separated, dried with calcium chloride and chloroform was removed. The distillation residue was allowed to crystallize. Isothiocyanates thus obtained were recrystallized from a suitable solvent.

In the case of amine hydrochlorides, thiophosgene was added into chloroform and the amine hydrochloride was dissolved in water. Solutions were mixed together at once and neutralized with powdered NaHCO_3 .

Table 3 and 4 contain the characterization of the prepared substances.

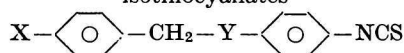
Results and discussion

4-(4-Nitrobenzylsulfonyl)aniline was synthesized from 4-nitrobenzyl bromide and sodium 4-acetamidobenzene sulfinate for the first time.

All isothiocyanates are crystalline substances with the exception of [(phenylthio)-methyl]phenyl isothiocyanate. Gasoline, light petroleum, carbon tetrachloride, and the mixture acetone—water (1 : 1) were used to crystallize the products in 52–88% yield. The lowest yield (32.6%) observed with 4-(4-nitrobenzylsulfonyl)phenyl isothiocyanate could be rationalized by the manifold crystallization from the acetone—water mixture.

Table 3

4-(4-Substituted benzylthio)- and 4-(4-substituted benzylsulfonyl)phenyl isothiocyanates

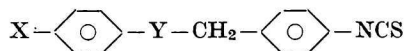


No.	X	Y	Formula	M	Calculated/found		Yield [%]	M.p. [°C]
					% N	% S		
XXI	H	S	$\text{C}_{14}\text{H}_{11}\text{NS}_2$	257.38	—	—	52.5	68–70
XXII	CH_3	S	$\text{C}_{15}\text{H}_{13}\text{NS}_2$	271.41	5.16 4.98	23.65 23.56	61.0	67–70
XXIII	Br	S	$\text{C}_{14}\text{H}_{10}\text{BrNS}_2$	336.27	4.17 ^a 4.31	19.07 19.16	86.3	96–98
XXIV	CN	S	$\text{C}_{15}\text{H}_{10}\text{N}_2\text{S}_2$	282.39	9.93 10.03	22.71 22.60	80.0	103–106
XXV	NO_2	S	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$	302.38	9.26 9.12	21.20 21.32	86.5	98–101
XXVI	NCS	S	$\text{C}_{15}\text{H}_{10}\text{N}_2\text{S}_3$	314.45	8.91 8.94	30.59 30.61	82.8	102–104
XXVII	H	SO_2	$\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}_2$	289.38	—	—	73.5	131–134
XXVIII	CH_3	SO_2	$\text{C}_{15}\text{H}_{13}\text{NO}_2\text{S}_2$	303.41	4.62 4.71	21.18 21.34	75.0	135–138
XXIX	NO_2	SO_2	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4\text{S}_2$	334.37	8.38 8.84	19.18 19.91	32.6	155–156
XXX	NCS	SO_2	$\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_3$	346.45	8.08 8.01	27.78 27.58	75.9	205–208

a) % Br calculated/found: 23.77
23.90

Table 4

4-[(4-Substituted phenylthio)methyl]-
and 4-[(4-substituted phenylsulfonyl)methyl]phenyl isothiocyanates



No.	X	Y	Formula	M	Calculated/found		Yield [%]	M.p. [°C] B.p. [°C/torr]
					% N	% S		
XXXI	H	S	C ₁₄ H ₁₁ NS ₂	257.38	5.43	24.85	64.2	186–189/3
XXXII	CH ₃	S	C ₁₅ H ₁₃ NS ₂	271.41	5.30	24.71	88.5	62–65
					5.16	23.65		
XXXIII	Cl	S	C ₁₄ H ₁₀ ClNS ₂	291.82	5.20	23.59	85.9	79–80
					—	—		
XXXIV	Br	S	C ₁₄ H ₁₀ BrNS ₂	336.27	4.17 ^a	19.07	87.2	80–81
					4.34	19.20		
XXXV	H	SO ₂	C ₁₄ H ₁₁ NO ₂ S ₂	289.38	4.83	22.10	86.5	153–155
					4.88	22.25		
XXXVI	CH ₃	SO ₂	C ₁₅ H ₁₃ NO ₂ S ₂	303.41	4.62	21.18	80.6	157–159
					4.78	21.02		
XXXVII	Cl	SO ₂	C ₁₄ H ₁₀ ClNO ₂ S ₂	323.82	4.34 ^b	19.85	83.3	150–151
					3.96	19.97		
XXXVIII	Br	SO ₂	C ₁₄ H ₁₀ BrNO ₂ S ₂	368.27	3.80 ^c	17.41	88.2	163–166
					3.75	17.55		

a) % Br calculated/found: 23.80
23.95

b) % Cl calculated/found: 10.90
10.68

c) % Br calculated/found: 21.64
21.82

Spectra of all synthesized isothiocyanates revealed medium intense bands at 936–944 cm⁻¹ assigned to the symmetric vibration of the —NCS group (Tables 5 and 6).

The investigated sulfone derivatives of isothiocyanates have the $\bar{\nu}_s(\text{SO})$ and $\bar{\nu}_{as}(\text{SO})$ bands located at 1160 ± 2 and 1331 ± 3 cm⁻¹, respectively. In both cases intense bands are involved, the $\bar{\nu}_s(\text{SO})$ being the more pronounced [23]. Absorption bands due to deformation vibrations of the CH₂ group lay in the 1414–1465 cm⁻¹ region and are, with many derivatives of little significance. Absorption bands belonging to the aromatic C=C vibrations of the isothiocyanates under study are in the ~1500 and ~1600 cm⁻¹ region and those in the sulfone series are doubled in the ~1600 cm⁻¹ region.

Furthermore, intense complex bands of $\bar{\nu}_{as}(\text{NCS})$ could be seen in the 2025–2197 cm⁻¹ region (Fig. 1). The highest band in the sulfide series of isothiocyanates is near 2100 cm⁻¹ (Table 5), that of 4-(4-substituted benzylsulfonyl)phenyl isothiocyanates at ~2045 cm⁻¹. The absorption spectra of 4-[(4-substituted phenylsulfonyl)methyl]phenyl isothiocyanates resemble closely those of sulfidic isothiocyanates indicating thus that the NCS group is not influenced by the electron effects of substituents attached to the methylene group

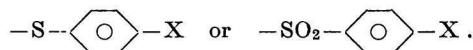


Table 5

Infrared and ultraviolet spectra of 4-(4-substituted benzylthio)- and 4-[(4-substituted phenylthio)methyl]phenyl isothiocyanates

Compound	$\tilde{\nu}_s(\text{NCS})$ [cm ⁻¹]	$\tilde{\nu}_{as}(\text{NCS})$ [cm ⁻¹]	$\lambda_{1\max}$ [nm] log ϵ	$\lambda_{2\max}$ [nm] log ϵ	$\lambda_{3\max}$ [nm] log ϵ
XXI	937 m	2063 vw, 2113 vs	—	—	293 302
		2183 w			4.42 4.41
XXII	936 m	2063 vw, 2112 vs	220 ^a	—	294 303
		2181 w	4.59		4.45 4.43
XXIII	937 m	2073 vw, 2106 vs	220 ^a	—	292 302
		2185 w	4.58		4.43 4.41
XXIV ^b	939 m	2053 vw, 2101 vs	223	—	293 302
		2183 w	4.60		4.44 4.42
XXV ^c	939 m	2061 vw, 2095 vs	222 ^a	276 ^a	290 301 ^a
		2184 vw	4.52		4.52 4.47
XXVI	939 m	2068 vw, 2107 vs	223 ^a	276	291 303 ^a
		2182 vw	4.75 4.53		4.60 4.50
XXXI	939 m	2065 vw, 2114 vs	225	259 ^a 274	284 —
		2183 w	4.56 4.26	4.35	4.32
XXXII	939 m	2065 vw, 2115 vs	224	256 ^a 274	284 —
		2182 w	4.58 4.26	4.36	4.33
XXXIII	938 m	2055 vw, 2115 vs	224	260 ^a 274	284 —
		2179 w	4.58 4.36	4.41	4.37
XXXIV	938 m	2070 vw, 2113 vs	224	260 ^a 273	285 —
		2182 w	4.58 4.37	4.43	4.39

s — strong, w — weak, m — medium, vs — very strong, vw — very weak
a) shoulder, b) $\tilde{\nu}_{\text{N}=\text{N}} = 2233$ s; c) $\tilde{\nu}_{\text{N}(\text{O}_2)} = 1354$ vs; $\tilde{\nu}_{\text{as}(\text{NO}_2)} = 1539$ s.

Table 6

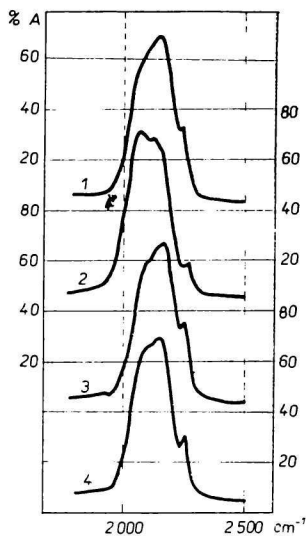
Infrared and ultraviolet spectra of 4-(4-substituted benzylsulfonyl)- and 4-[(4-substituted phenylsulfonyl)methyl]phenyl isothiocyanates

Compound	$\tilde{\nu}_s(\text{NCS})$ [cm ⁻¹]	$\tilde{\nu}_s(\text{S=O})$ [cm ⁻¹]	$\tilde{\nu}_{as}(\text{S=O})$ [cm ⁻¹]	$\tilde{\nu}_{as}(\text{NCS})$ [cm ⁻¹]	$\lambda_{1\max}$ [nm] log ϵ	$\lambda_{2\max}$ [nm] log ϵ
XXVII	944 m	1158 vs	1332 vs	2035 vs, 2080 w	228	277 ^a 293
				2194 w	4.49	4.25 4.40
XXVIII	942 m	1158 vs	1330 vs	2038 vs, 2077 vw	227	279 ^a 293
				2193 w	4.55	4.35 4.40
XXIX ^b	938 m	1160 vs	1335 m	2025 vs, 2075 vw	228	279 292
				2197 w	4.26	4.34 4.31
XXX	942 s	1161 vs	1333 vs	2055 vs, 2096 w	227	276 ^a 289
				2191 w	4.68	4.51 4.57
XXXV	940 m	1161 vs	1328 s	2063 w, 2114 vs	227	274 286
				2188 w	4.56	4.36 4.33
XXXVI	941 m	1158 vs	1328 s	2065 w, 2114 vs	228	276 287
				2188 w	4.63	4.38 4.36
XXXVII	938 m	1162 vs	1334 s	2053 w, 2103 vs	227	275 286
				2190 w	4.64	4.35 4.33
XXXVIII	942 m	1162 vs	1334 s	2065 w, 2105 vs	228	276 287
				2187 w	4.65	4.37 4.35

s — strong, w — weak, m — medium, vs — very strong, vw — very weak.
a) shoulder, b) $\tilde{\nu}_{\text{S}(\text{NO}_2)} = 1356$ s; $\tilde{\nu}_{\text{as}(\text{NO}_2)} = 1538$ m.

Fig. 1. Infrared absorption bands $\bar{\nu}_{\text{as}}(\text{NCS})$ in the 2000–2500 cm^{-1} region.

1. 4-(benzylthio)phenyl isothiocyanate; 2. 4-benzylsulfonylphenyl isothiocyanate; 3. 4-[(phenylthio)methyl]phenyl isothiocyanate; 4. 4-[(phenylsulfonyl)methyl]phenyl isothiocyanate.



Absorption bands of the CH_2 group are in the 2840–2878 cm^{-1} region for $\bar{\nu}_{\text{s}}(\text{CH}_2)$ and 2917–2943 cm^{-1} for $\bar{\nu}_{\text{as}}(\text{CH}_2)$; the symmetric vibrations of the CH_2 group are either little significant, or do not appear at all.

When contrasting the ultraviolet absorption spectrum of 4-(4-substituted benzylthio)phenyl isothiocyanate (derivatives XXI–XXVI; Table 5) with that of phenyl isothiocyanate it becomes evident that the $\text{X}-\text{C}_6\text{H}_4-\text{CH}_2-\text{S}-$ group is responsible for the bathochromic shift of the absorption band (λ_{max} 277 → 290 nm) associated with the phenyl isothiocyanate conjugated system [24]. The nature of the substituent X does not virtually affect the position of absorption bands (Table 5).

Absorption bands in the 273–276 and 284–287 nm regions of the 4-[(4-substituted phenylthio)methyl]phenyl isothiocyanates (derivatives XXXI–XXXIV; Table 5) and 4-[(substituted phenylsulfonyl)methyl]phenyl isothiocyanates (derivatives XXXV–XXXVIII; Table 6) could be ascribed to the $\pi \rightarrow \pi^*$ transition associated with the electron transfer as a result of conjugation of the isothiocyanate group with aromatic ring.

An absorption band at ~ 227 nm ($\log \epsilon \sim 4.5$), a shoulder at 276–279 nm ($\log \epsilon \sim 4.4$) and a band at 289–293 nm ($\log \epsilon \sim 4.4$) are indicative of 4-(4-substituted benzylsulfonyl)phenyl isothiocyanates (derivatives XXVII–XXX; Table 6). The absorption maximum at about 290 nm is strongly bathochromically and hyperchromically shifted in regard to unsubstituted benzyl phenyl sulfone (λ 265; $\log \epsilon$ 3.03 [25]), what might be due to an interaction between the NCS and SO_2 groups.

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