

Isothiocyanates (XXIV)*

Synthesis and Identification of 4-(*p*-Terphenyl)isothiocyanates and Their Intermediates

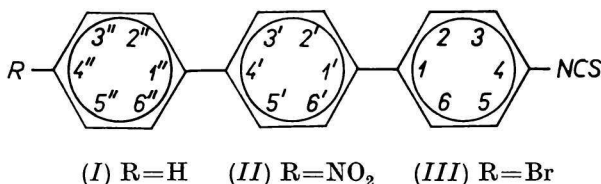
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This paper deals with the synthesis of three up to date not described 4-(*p*-terphenyl)isothiocyanates and their six intermediates, two of which having not been described, too. A procedure was developed to identify *p*-terphenyl derivatives by means of thin layer chromatography on alumina, as well as by gas chromatography. Infra-red and ultra-violet spectra were taken of the synthesized 4-(*p*-terphenyl)isothiocyanates.

Isothiocyanates derived from *p*-terphenyl were hitherto not described in the literature:



Intermediates for the synthesis of 4-(*p*-terphenyl)isothiocyanate (I), 4''-nitro-4-(*p*-terphenyl)isothiocyanate (II) and 4''-bromo-4-(*p*-terphenyl)isothiocyanate (III) presented in this paper were in part known.

In spite of the fact that a large amount of *p*-terphenyl derivatives have been recently described, there are still quick and selective methods lacking to identify these stuffs.

Paper chromatography was used to separate sulfo acids of *o*-, *m*- and *p*-terphenyl [1]. The mixture of the mentioned isomers was separated also gas chromatographically [2]. *p*-Terphenyl and 4-(*p*-terphenyl)amine were identified by ultra-violet spectra [3].

In this paper thin layer chromatography on alumina, gas chromatography, infra-red and ultra-violet spectra were found to be useful tools for checking the purity of 4- and 4,4''-substituted derivatives of *p*-terphenyl.

* Part XXIII see *Chem. zvesti* 22, 439 (1968).

Experimental

4-(*p*-Terphenyl)amine, an intermediate needed for the further synthesis of 4-(*p*-terphenyl)isothiocyanate (*I*) was prepared starting from azobenzene hydrochloride and biphenyl in carbon sulfide in the presence of aluminium chloride [4, 5], as well as from 4-nitro-*p*-terphenyl by reduction with stannous chloride in ethanol and concentrated hydrochloric acid [6]. 4''-Nitro-4-(*p*-terphenyl)isothiocyanate (*II*) was prepared from *p*-terphenyl *via* 4,4''-dinitro-*p*-terphenyl [7] and 4''-nitro-4-(*p*-terphenyl)amine [8, 9]. The synthesis of 4''-bromo-4-(*p*-terphenyl)isothiocyanate (*III*) was performed *via* 4''-nitro-4-(*p*-terphenyl)bromide and 4''-bromo-4-(*p*-terphenyl)amine.

4''-Nitro-4-(p-terphenyl)bromide

4''-Nitro-4-(*p*-terphenyl)amine (7 g, 0.024 mol.) was dissolved in a mixture of glacial acetic acid (490 ml) and 31 % hydrobromic acid (96 ml, 0.465 mol.) at elevated temperature. This solution was cooled to 0 °C and the suspension thus formed was diazoted with sodium nitrite (3.3 g, 0.048 mol.) in water (60 ml) and poured into another suspension consisting of cuprous bromide (18.9 g, 0.132 mol.) in 31 % hydrobromic acid (37 ml, 0.179 mol.) cooled to 0 °C. The reaction mixture was then decomposed at 100 °C, cooled and diluted with an equal amount of water. The precipitate was filtered off and washed successively with concentrated hydrobromic acid (30 ml), water and a small amount of ethanol. The yellow 4''-nitro-4-(*p*-terphenyl)bromide was crystallized from toluene and obtained in 55 % yield (4.65 g). Analysis and melting point are given in Tab. 1.

4''-Bromo-4-(p-terphenyl)amine

A solution of crystalline stannous chloride (40 g, 0.18 mol.) in concentrated hydrochloric acid (35 ml, 0.41 mol.) was added to a suspension of 4''-nitro-4-(*p*-terphenyl)bromide (4.5 g, 0.013 mol.) in 96 % ethanol (800 ml) at the boiling point temperature. The stirred reaction mixture was kept boiled under a reflux condenser, the colourless, clear solution was cooled, the crystalline 4''-bromo-4-(*p*-terphenyl)ammonium chloride was filtered off and washed with water. The amine was set free by heating with concentrated ammonium hydroxide. After cooling the precipitated 4''-bromo-4-(*p*-terphenyl)amine was filtered off, washed and air dried. Yield 3.45 g (84 %) after crystallization from ethanol. Both analysis and melting point are listed in Tab. 1.

A general procedure for preparing 4-(p-terphenyl)isothiocyanates

A solution of either 4-(*p*-terphenyl)amine (0.02 mol.), or appropriate 4''-substituted 4-(*p*-terphenyl)amine in 800 ml chloroform was added, while vigorously stirred to a suspension of 300 ml water, 100 ml chloroform, 1.7 ml (2.56 g, 0.022 mol.) thiophosgene and 2.4 g (0.024 mol.) calcium carbonate at 30 °C. Stirring of the reaction mixture was continued for 3 hours at this temperature and the unreacted calcium carbonate was filtered off. Chloroform and the remaining thiophosgene were removed by steam distillation. The crude isothiocyanate which has been separated from the solution was filtered off, air dried and crystallized from chloroform, adding charcoal and a small amount of alumina. Products of this reaction were crystallized from chloroform — light petroleum and their melting points are listed in Tab. 1.

Table 1
Physicochemical properties and analyses of the synthesized derivatives of *p*-terphenyl

No.	Substituent		Molecular formula	M	Melting point °C		Yield %	Calculated		Chromatography			
	4-	4''-			reported	found		found		thin layer			gas
								% N	% S	R_F^b	fluorescence in UV light	V_R^c	V_R^d
1	—NH ₂	—	C ₁₈ H ₁₅ N	245.31	197—198 [12]	198	80			0.18	blue	—	3.52
2	—NCS	—	C ₁₉ H ₁₃ NS	287.36		183—185	79	4.88	11.16	0.83	violet	—	6.58
3	—NO ₂	—	C ₁₈ H ₁₃ O ₂ N	275.29	208 [3]	208		4.75	11.32	0.64	yellow	—	4.57
4	—NO ₂	—NO ₂	C ₁₈ H ₁₂ O ₄ N	320.29	278—279 [7]	278—279	33	8.75		0.30	yellow	—	—
	—NH ₂	—NO ₂	C ₁₈ H ₁₄ O ₂ N ₂	290.31	301 [13]	301	66	8.61		0.06	brown	—	—
6	—NCS	—NO ₂	C ₁₉ H ₁₂ O ₂ N ₂ S	332.36		221—222 ^a)	71	9.65	9.64	0.60	yellow	—	—
7	—Br	—	C ₁₈ H ₁₃ Br	309.20	231—232 [8]	231—232		9.25	9.77	0.79	blue	—	2.60
8	—Br	—NO ₂	C ₁₈ H ₁₂ BrNO ₂	354.20		299—300		3.95		0.62	orange	—	—
9	—NH ₂	—Br	C ₁₈ H ₁₁ BrN	324.22		280—282	84	3.88		0.20	blue	—	—
10	—Br	—NCS	C ₁₉ H ₁₂ BrNS	366.27		247—249	73	4.32	8.75	0.82	blue-violet	—	—
								4.25	8.58		-violet	1.00	1.00
11	<i>p</i> -terphenyl		C ₁₈ H ₁₄	230.29	214 [14]		—	3.82		0.83	blue-violet	0.88	—
12	<i>m</i> -terphenyl		C ₁₈ H ₁₄	230.29	87 [15]		—	3.71		0.81	blue-violet	0.34	—
13	<i>o</i> -terphenyl		C ₁₈ H ₁₄	230.29	57 [16]		—				blue-violet		—

a) Melting point is dependent on mesomorphic and polymorphic changes.

b) Developing system: Carbon tetrachloride—chloroform in the ratio 2 : 1, adsorbent Al₂O₃ (grade III according to Brockmann).

c) Values obtained at 175 °C.

d) Values obtained at 215 °C.

Identification of terphenyl compounds by thin layer chromatography

For chromatographic determination of terphenyl derivatives loose layer chromatography on alumina (grade III according to Brockmann) was used, the activity of alumina being previously tested with azo dyes [10]. Thin layers of standard thickness 0.75 mm were coated on 11 × 4 cm glass plates. Tetrachloromethane and chloroform in the ratio 2 : 1 were found to be a convenient developing system. When visualized in the ultra-violet light the spots revealed a characteristic fluorescence. Proper data concerning the particular terphenyl compound are listed in Tab. 1.

Separation of terphenyl derivatives by gas chromatography

Because of the impossibility of some terphenyl derivatives to be separated and identified by thin layer chromatography having their R_F values very close, as in the case of e. g. *p*-terphenyl and brominated *p*-terphenyls, a procedure using gas chromatography was developed. A gas chromatograph Fractovap, model C (Carlo Erba, Milano) was used; this apparatus was equipped with a flame ionization detector, the injection system was made of borosilicate glass tube. Working conditions were as follows: the column temperature 175 and 215 °C, column length 80 cm, inner diameter of the column 3 mm, stationary phase 5 % silicone grease SE 301 over Chromosorb W, carrier gas — nitrogen. Elution data are given in Tab. 1. The separation is evident from Fig. 1.

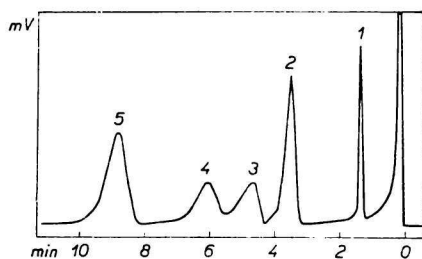


Fig. 1. Chromatogram of the monosubstituted derivatives of terphenyl.

1. *p*-terphenyl; 2. 4-(*p*-terphenyl)l bromide; 3. 4-(*p*-terphenyl)amine; 4. 4-nitro-*p*-terphenyl; 5. 4-(*p*-terphenyl)isothiocyanate.

Column: 5 % silicone grease SE-301 over silanecoated Chromosorb at 215 °C.

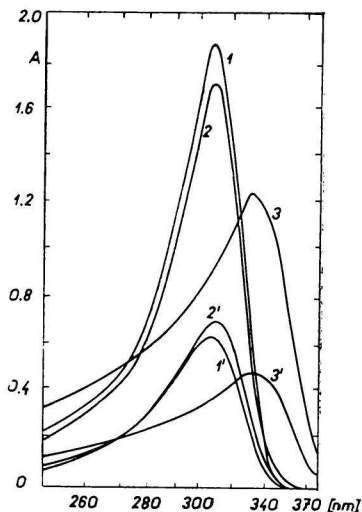


Fig. 2. Ultra-violet spectra of 4-(*p*-terphenyl)isothiocyanates.

1. and 1'. 4-(*p*-terphenyl)isothiocyanate; 2. and 2'. 4''-bromo-4-(*p*-terphenyl)isothiocyanate; 3. and 3'. 4''-nitro-4-(*p*-terphenyl)isothiocyanate.

1., 2. and 3. $2.5 \cdot 10^{-5}$ M. Solution in chloroform; 1', 2'. and 3'. $2 \cdot 10^{-5}$ M solution in chloroform.

Spectral measurements in ultra-violet and infra-red region

Measurements in the ultra-violet region were taken with a Perkin—Elmer spectrophotometer, model 450 in the 250—340 nm, eventually 420 nm range in 10 mm Suprasil cells. Preparations were measured in a chloroform solution in $2 \cdot 10^{-5}$ and $2.5 \cdot 10^{-5}$ M concentration. Values are given in absorbancy units.

With 4-(*p*-terphenyl)isothiocyanates the absorption maxima were measured as follows: 4-(*p*-terphenyl)isothiocyanate at 307.1 nm, 4''-nitro-4-(*p*-terphenyl)isothiocyanate at 330.5 nm, 4''-bromo-4-(*p*-terphenyl)isothiocyanate at 308.3 nm. Ultra-violet spectra of these isothiocyanates are plotted in Fig. 2.

Infra-red spectra of 4-(*p*-terphenyl)isothiocyanates were run in chloroform solutions in 700—3600 cm^{-1} range with a UR-10 Zeiss spectrophotometer. In the case of 4-(*p*-terphenyl)isothiocyanate a cell of 0.187 mm in width was used. In regard to the limited solubility of the substituted 4-(*p*-terphenyl)isothiocyanates a KBr cell 1.03 mm wide was used for the nitro derivative and NaCl cell 2.68 mm wide for the bromo derivative.

Results and discussion

The synthesis of terphenyl compounds when compared with this of analogous biphenyl derivatives is believed to be more difficult considering the feature which is ascribed to substances in the transition to higher molecular weights, mainly the lower solubility. General methods given in the literature were used by the authors to synthesize terphenyl compounds, the known properties of the described polyphenylene derivatives being properly taken into consideration. The purification of intermediates and final products was done by means of physicochemical methods and the substances were identified quickly by thin layer chromatography on alumina, gas chromatography and spectrophotometric estimation as described above.

As seen from R_F values given for the thin layer chromatography on alumina (Tab. 1), the separation of terphenyl compounds is possible in most cases. Good results were obtained when identifying reaction mixtures from nitration of *p*-terphenyl, from reduction of 4-nitro-*p*-terphenyl to 4-(*p*-terphenyl)amine, from the selective reduction of 4,4''-dinitroterphenyl to 4''-nitro-4-(*p*-terphenyl)amine and from the condensation of amino substituted terphenyls with thicphosgene to the particular isothiocyanates. Of derivatives described in this paper this method failed only with the separation of *p*-terphenyl and bromo terphenyls and even the combination of more polar solvents (*n*-heptane—acetone, xylene—acetone, *n*-heptane—benzene) used as a mobile phase was found to be unsuccessful.

As seen from the gas chromatography elution data (Tab. 1) this method is a convenient one to complement the thin layer absorption chromatography on alumina in those cases, where the separation by thin layer chromatography could not be achieved. Very good results were obtained with the separation of *o*-, *m*- and *p*-terphenyls, as well as with the unsubstituted derivatives of *p*-terphenyl, as shown in Fig. 1. Our method of separation of isomeric terphenyls when compared with those so far known [2] was shown to be advantageous because of the lower temperature, shorter column and shorter time used. These conditions were effected by applying a low amount of the stationary phase on the adsorbent.

Spectrophotometric measurements of *p*-terphenyl derivatives in the ultra-violet region revealed accordance of the shift of the absorption maximum with the nature of substituents. This is in agreement with the data reported in the literature [3] for *p*-terphenyl, 4-(*p*-terphenyl)amine and 4''-amino-4-(*p*-terphenyl)amine as being 275, 306 and 315 nm, respectively.

Table 2

Characteristic vibrations of the synthesized 4-(*p*-terphenyl)isothiocyanates given in cm^{-1}

Isothiocyanate	$\tilde{\nu}_{\text{sym}}$ NCS	$\tilde{\nu}_{\text{asym}}$ NCS	$\tilde{\nu}_{\text{C}=\text{C}}$ (arom.)	$\tilde{\nu}_{\text{C}-\text{H}}$ (arom.)	$\tilde{\nu}_{\text{C}-\text{H}}$ (out of plane mono- arom.)	$\tilde{\nu}_{\text{C}-\text{H}}$ (aliph.)
4-(<i>p</i> -terphenyl)- isothiocyanate	935 m	2180 vw 2118 s 2055 sh	1603 w 1506 w 1489 s	3018 w 3037 vw 3076 vw	856 w 929 s 702 m	—
4''-nitro-4- -(<i>p</i> -terphenyl)- isothiocyanate	943 w	2185 w 2110 s 2040 sh	1603 vs 1507 m 1489 s	—	880 s 858 s 832 w	1394 s 1348 vs
4''-bromo-4- -(<i>p</i> -terphenyl)- isothiocyanate	946 w	2182 w 2110 s 2040 sh	1607 s 1495 m 1484 m	—	880 m 863 vw	1392 s

s = strong, vs = very strong, m = medium, w = weak,
vw = very weak, sh = shoulder.

In infra-red spectra the isothiocyanate group of the examined isothiocyanates exhibited bands in 3 regions: $\tilde{\nu}_{\text{as}}$ NCS at 2.180, 2.110 and 2.050 cm^{-1} and $\tilde{\nu}_{\text{sym}}$ NCS at 940 cm^{-1} . Aromatic isothiocyanates as e. g. *p*-nitrophenylisothiocyanate and phenylisothiocyanate show a frequency shift up to 36 cm^{-1} [11]. Deactivation substituents (NO_2 , Br) lower the first maximum also in *p*-terphenylisothiocyanates when compared with this of the unsubstituted derivative. The lowering from 2.055 to 2.040 cm^{-1} evidences the influence of the substituent on the character of the NCS group which is bonded through a conductive *p*-terphenyl system. Characteristic vibrational data of the synthesized 4-(*p*-terphenyl)isothiocyanates are listed in Tab. 2.

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IZOTIOKYANÁTY (XXIV)
SYNTÉZA A IDENTIFIKÁCIA 4-(*p*-TERFENYLYL)IZOTIOKYANÁTOV A ICH
MEDZIPRODUKTOV

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Pripravili sme tri izotiokyanáty *p*-terfenylového typu v literatúre zatiaľ neopísané, a to 4-(*p*-terfenylyl)izotiokyanát s b. t. 184—185 °C, 4''-nitro-4-(*p*-terfenylyl)izotiokyanát s b. t. 221—222 °C a 4''-bróm-4-(*p*-terfenylyl)izotiokyanát s b. t. 248—249 °C, ako aj dva medziprodukty: 4''-nitro-4-(*p*-terfenylyl)bromid s b. t. 299—300 °C a 4''-bróm-4-(*p*-terfenylyl)amín s b. t. 280—282 °C. Uvedené zlúčeniny sme identifikovali analýzou, infračervenými a ultrafialovými spektrami, ako aj pomocou chromatografie na tenkej vrstve kyslíčnika hlinitého. Monosubstituované deriváty *p*-terfenylu, a to 4-(*p*-terfenylyl)bromid, 4-(*p*-terfenylyl)amín, 4-nitro-*p*-terfenyl a 4-(*p*-terfenylyl)izotiokyanát sme rozdeľovali pomocou plynovej chromatografie.

ИЗОТИОЦИАНАТЫ (XXIV)
СИНТЕЗ И ИДЕНТИФИКАЦИЯ 4-(*n*-ТЕРФЕНИЛИЛ)ИЗОТИОЦИАНАТОВ
И ИХ ПРОМЕЖУТОЧНЫХ ПРОДУКТОВ

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Были получены 3 изотиоцианата *n*-терфенильного типа, до сих пор не описанные в литературе, а именно: 4-(*n*-терфенилил)изотиоцианат с температурой плавления 184—185°, 4''-нитро-4-(*n*-терфенилил)изотиоцианат с температурой плавления 221—222° и 4''-бром-4-(*n*-терфенилил)изотиоцианат с температурой плавления 248—249° и 2 промежуточных продукта: 4''-нитро-4-(*n*-терфенилил)бромид с температурой плавления 299—300° и 4''-бром-4-(*n*-терфенилил)амин с температурой плавления 280—282°. Описанные соединения были идентифицированы анализом, инфракрасными и ультрафиолетовыми спектрами, а также хроматографией на тонком слое окиси алюминия. Монозамещенные производные *n*-терфенила: 4-(*n*-терфенилил)бромид, 4-(*n*-терфенилил)амин 4-нитро-*n*-терфенил и 4-(*n*-терфенилил)изотиоцианат были разделены с помощью газовой хроматографии.

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