

# Isothiocyanates. XXV. Synthesis, Infra-red and Ultra-violet Spectra of Isothiocyanatodiphenyloxides

A. MARTVOŇ and K. ANTOŠ

*Department of Organic Chemistry, Slovak Technical University,  
Bratislava 1*

Received July 2, 1968

In revised form November 21, 1968

In this paper, the synthesis of a series of 4-substituted derivatives of 4-isothiocyanatodiphenyloxide is described. The NCS group is influenced by substituents to a small extent ( $\rho = -15.8$ ) when compared with other conductive systems as can be concluded from the correlation of absorption maxima  $\nu_{\text{as}}(\text{NCS})$  in the  $2060 \text{ cm}^{-1}$  range with the Hammett  $\sigma_p$  constant of the substituent. The evaluation of the mutual interaction is also based on ultra-violet spectra.

In continuation of our previous papers [1—4] in which the interaction of the NCS group with other functional groups throughout longer conjugation systems was investigated, our attention has been paid to the diphenyloxide conjugated system.

Similarly as in our previous papers, we try to examine the character of the NCS group, as well as its interaction with other groups which are attached to it through the diphenyloxide system on the basis of infra-red and ultra-violet spectra. From the above-mentioned papers it follows that the electron effects in longer conjugated systems are suppressed when compared with those of benzene. The overall view of our study to be comprehended it was useful to examine even the diphenyloxide conjugated system, since the opinion as to the character of conjugation of this system is being disunited [5, 6].

## Experimental

Amines prepared by reduction of nitro derivatives were used as a starting material in the synthesis of isothiocyanatodiphenyloxides.

4-Nitrodiphenyloxide was prepared according to *Haussermann* [7]. The preparation of 4-methyl-4'-nitrodiphenyloxide is given in [8, 9]; that of 4,4'-dinitrodiphenyloxide in [10]. 4-Aminodiphenyloxide, 4-methyl-4'-aminodiphenyloxide, 4-chloro-4'-aminodiphenyloxide and 4-bromo-4'-aminodiphenyloxide resulted from the reduction of the appropriate nitro derivatives with iron and hydrochloric acid in ethanol [7].

4-Nitro-4'-aminodiphenyloxide was prepared by reduction of the 4,4'-dinitro derivative with sodium sulfite in acetone [11]; 4,4'-diaminodiphenyloxide was synthesized from the dinitro derivative by reduction with zinc and hydrochloric acid [12].

### *Preparation of isothiocyanates*

The proper amino derivatives [17] were treated with thiophosgene to give 4-substituted-4'-isothiocyanatodiphenyloxides similarly as reported in [1].

The isolation of the final products which was different from the quoted procedure was performed as follows.

Table 1

List of synthesized isothiocyanatodiphenyloxides

No.	Compound	Molecular formula	M	Calculated/found			Yield %	m.p. [°C] b.p.
				% C	% H	% N		
1	4-isothiocyanatodiphenyl-oxide	C <sub>13</sub> H <sub>9</sub> NOS	227.27	68.27 68.12	3.98 3.81	6.16 6.38	86	40—41
2	4-methyl-4'-isothiocyanato-diphenyloxide	C <sub>14</sub> H <sub>11</sub> NOS	241.30	69.10 69.33	5.38 5.41	5.75 5.43	87	33—35
3	4-chloro-4'-isothiocyanato-diphenyloxide	C <sub>13</sub> H <sub>8</sub> ClNOS	261.72	59.65 59.71	3.08 3.19	5.35 5.33	51	190—195/0.7 torr
4	4-bromo-4'-isothiocyanato-diphenyloxide	C <sub>13</sub> H <sub>8</sub> BrNOS	306.18	50.99 60.18	2.63 2.41	4.37 4.23	50	205—209/0.7 torr
5	4-nitro-4'-isothiocyanato-diphenyloxide	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub> S	272.27	59.13 59.27	2.82 2.80	9.58 9.61	36	107—113
6	4,4'-diisothiocyanato-diphenyloxide	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> OS <sub>2</sub>	284.35	57.34 57.21	2.86 2.82	10.29 10.48	32	68—69.5

4-Chloro-4'-isothiocyanatodiphenyloxide and 4-bromo-4'-isothiocyanatodiphenyloxide were vacuum distilled at 190—195°C/0.7 torr and 200—205°C/0.7 torr, respectively. The remaining isothiocyanates listed in Table 1 were dissolved in light petroleum, the single solutions were then purified over an alumina column and finally, the products were separated in a crystalline form the external dry ice cooling being applied.

#### Measurement of infra-red spectra

Infra-red spectra of the synthesized isothiocyanatodiphenyloxides were measured in a chloroform solution in 0.2 M concentration. The measurement was performed with a UR-10 Zeiss spectrometer in the 3600—700 cm<sup>-1</sup> range. The apparatus was calibrated with a polystyrene film.

#### Measurement of ultra-violet spectra

Ultra-violet spectra were measured in a *n*-heptane solution with an ORD/UV-JASCO spectrophotometer in 10<sup>-5</sup> M concentration.

### Discussion

The synthesis of intermediates of diphenyloxide type was done by condensation of *p*-nitrochlorobenzene with the proper *p*-substituted sodium phenolate. The homogeneity of the reaction medium to be attained a small excess of *p*-substituted phenol was added to the reaction mixture. A good reaction course was observed with potassium phenolate and potassium *p*-cresolate the yield being 51.5 and 64%. Upon condensation with halophenols with *p*-nitrochlorobenzene the yield was found to be lower. Due to their deactivation effect, halogens evidently lower the reactivity of the phenolate ion as a result of its decreased nucleophilicity.

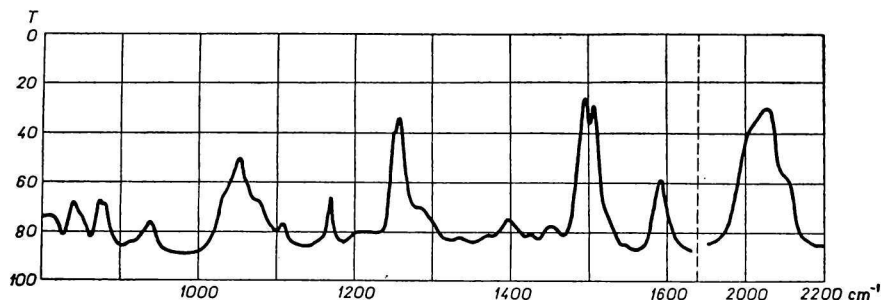


Fig. 1. Infra-red spectrum of 4-isothiocyanatodiphenyloxide.

It was found out that the condensation of *p*-nitrochlorobenzene with potassium *p*-nitrophenolate does not occur in contrast to the fact that this method of preparation of 4,4'-dinitrodiphenyloxide is given in the literature [7]. In attempting to prepare this derivative numerous methods [7, 13, 14] were used without any success. However, this derivative was prepared in good yield by condensation of *p*-nitrophenol with *p*-nitrochlorobenzene in the presence of fused  $K_2CO_3$  in nitrobenzene [10]. Nitro derivatives were reduced to proper amino derivatives; iron

Table 2  
Infra-red frequency values of isothiocyanates

No.	X	$\delta(C-H)$ ( $cm^{-1}$ )	$\nu_s(NCS)$ ( $cm^{-1}$ )	$\delta(C-H)$ $\delta(C-O)$ ( $cm^{-1}$ )	$\nu_{as}(C-O-C)$ ( $cm^{-1}$ )	$\nu(C=C)$ ( $cm^{-1}$ )	$\nu_{as}(NCS)$ ( $cm^{-1}$ )
1	H	832	937	1025	1258	1495	2080
		852		1075		1505	2110
		875		1105		1592	2195
				1165			
2	CH <sub>3</sub>	832	937	1020	1255	1500	2085
		852		1105		1605	2110
		875		1165			2190
3	Cl	832	937	1015	1250	1490	2075
		852		1090		1505	2110
		875		1165		1590	2190
4	Br	832	937	1017	1250	1594	2073
		852		1105		1618	2110
		875		1165			2190
5	O <sub>2</sub> N	850	937	1017	1250	1594	2073
		880		1105		1618	2110
				1165			2190
6	SCN	832	937	1015	1250		
		852		1105		1590	2073
		875		1165		1600	2110
							2190

and granulated tin in acid media were used as reducing agents. A partial reduction was performed with sodium sulfide. The yield of reduction is in good accordance with that given in the literature.

The synthesis of isothiocyanatodiphenyloxides was performed with thiophosgene. Isothiocyanatodiphenyloxides described in this paper are substances in the boundary between solid and liquid phase at normal conditions: their melting points are quite low and their isolation in a pure state was therefore a bit troublesome. Their distillation was unsuccessful as a consequence of their low volatility at higher temperatures. It was necessary to purify their light petroleum solutions over alumina and the crystallization was provoked by dry ice cooling. The halosubstituted isothiocyanates failed to give crystalline products while applying the same method and they were, therefore, vacuum distilled.

Infra-red spectra of isothiocyanatodiphenyloxides exhibit a strong absorption in the  $1600-800\text{ cm}^{-1}$  range as exemplified by 4-isothiocyanatodiphenyloxide in Fig. 1. Infra-red spectra of the remaining isothiocyanates are of similar pattern; in addition, they show absorption bands associated with the proper functional groups (Table 2). Absorption bands in the  $875-830\text{ cm}^{-1}$  region are attributed to the out-of-plane deformation vibrations of C—H aromatic. The absorption band at  $930\text{ cm}^{-1}$   $\nu_s(\text{NCS})$  is not on the substituent dependent. There are some bands in the  $1200-1000\text{ cm}^{-1}$  region associated with both in-plane C—H deformation vibrations and C—O stretching vibrations. In the spectra of all investigated diphenyloxide derivatives characteristic bands for  $\nu_{\text{as}}(\text{C—O—C})$  were observed at  $1250\text{ cm}^{-1}$  [15, 16]. C=C Vibrations of the aromatic nucleus were found in the  $1400-1600\text{ cm}^{-1}$  region. Three peaks at  $2060$ ,  $2100$  and  $2180\text{ cm}^{-1}$  (Table 2) both latter being substituent unaffected are indicative for the isothiocyanate group. It was possible to correlate frequencies attributable to the absorption band at  $2060\text{ cm}^{-1}$  with  $\sigma_p$  constants. The linear dependence resulting from this correlation is plotted in Fig. 2.

A good correlation is evidenced by the correlation coefficient value  $r = 0.968$ . A low slope of this linear dependence ( $\rho = -15.8$ ) when compared with that of isothiocyanatostilbenes ( $\rho = -23.7$ ) [1], isothiocyanatoazobenzenes ( $\rho = -19.8$ ) [4], isothiocyanatobiphenyls ( $\rho = -20.1$ ) [3] and isothiocyanatodiphenylsulfides ( $\rho =$

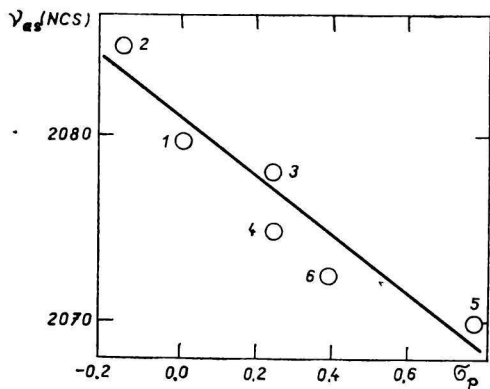


Fig. 2. The dependence of  $\nu_{\text{as}}(\text{NCS})$  on the  $\sigma_p$  constant of substituents in 4-substituted-4'-isothiocyanatodiphenyloxides. Single dots represent substituents in the same order as given in Tables 1—3.

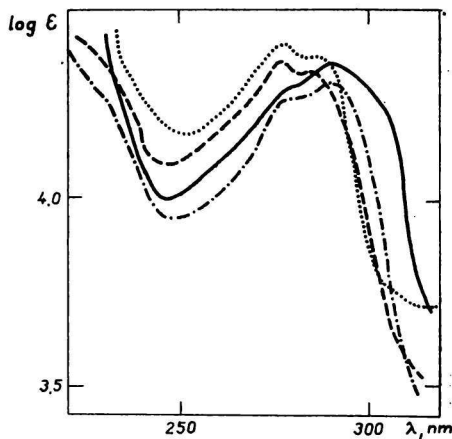


Fig. 3. Ultra-violet spectra  
of isothiocyanatodiphenyloxides.

- ... 4-isothiocyanatodiphenyloxide,
- 4-methyl-4'-isothiocyanatodiphenyloxide,
- 4,4'-diisothiocyanatodiphenyloxide,
- .- 4-nitro-4'-isothiocyanatodiphenyloxide.

= -19.7) [2] suggests that the diphenyloxide system markedly suppresses the electrone effects of the mutual interaction of two functional groups.

Ultra-violet spectra of isothiocyanatodiphenyloxides investigated are characterized by two absorption bands at 270 and 220 nm (Fig. 3, Table 3). A well pronounced bathochromic effect of the absorption maximum at 270 nm is observed only when  $\text{NO}_2$  or NCS group is present, whilst the remaining groups do not affect its position. The absorption band at 220 nm appears as an inflexion because of the  $\pi \rightarrow \pi^*$  transition of the benzene ring which strongly absorbs at shorter wavelength. As seen in Fig. 3, the *K*-band is split; this has been observed even in other aromatic

Table 3

Ultra-violet characteristic data of isothiocyanates

No.	Substituent	$\lambda_{\text{max}}$ (nm)	log $\epsilon$	$\lambda_{\text{max}}$ (nm)	log $\epsilon$
1	H	277	4.41	224	4.50
2	$\text{CH}_3$	277	4.37	227	4.41
3	Cl	278	4.36	230	4.43
4	Br	277	4.40	226	4.45
5	$\text{O}_2\text{N}$	290	4.35	225	4.45
6	SCN	291	4.30	231	4.25

isothiocyanates [1, 4]. The absorption maximum of isothiocyanatodiphenyloxides with an activation substituent is distinguished by higher extinction of the band at shorter wavelengths, whereas deactivation substituents cause an inverse phenomenon, *i.e.* they suppress the extinction of the band at shorter wavelengths and raise this one at longer wavelengths. To explain the observed phenomenon a more detailed study of the ultra-violet spectra of aromatic isothiocyanates would be needed.

## References

1. Martvoň A., Antoš K., *Chem. Zvesti* **22**, 102 (1968).
2. Uher M., Antoš K., *Chem. Zvesti* **22**, 439 (1968).
3. Antoš K., Stankovský Š., Kardoš M., *Collect. Czech. Chem. Commun.*, in press.
4. Martvoň A., Antoš K., Sticzay T., *Collect. Czech. Chem. Commun.*, in press.
5. Litvinenko L. M., Češko R. S., Hoffmann A. D., *Ž. Obšč. Chim.* **27**, 831 (1957).
6. Litvinenko L. M., *Izv. Akad. Nauk SSSR, Otd. Chim. Nauk* **1962**, 1737.
7. Haeussermann C., Teihmann H., *Ber.* **29**, 1447 (1896).
8. Raiford L. C., Colbert J. C., *J. Amer. Chem. Soc.* **48**, 2659 (1926).
9. Jones C. W., Cook W. T., *J. Amer. Chem. Soc.* **38**, 1544 (1916).
10. USSR Patent 17 4189 (27. 8. 1965).
11. Litvinenko L. M., Češko R. S., Hoffmann A. D., *Ž. Obšč. Chim.* **97**, 758 (1957).
12. Hoffmeister K., *Justus Liebigs Ann. Chem.* **159**, 208 (1871).
13. Hoffmeister K., *Justus Liebigs Ann. Chem.* **159**, 719 (1871).
14. Maiche A., Murat M., *Compt. Rend.* **154**, 715 (1912).
15. Unguande H. E., Picket E. E., Rubin L., *J. Org. Chem.* **16**, 1318 (1951).
16. Dahlard M., Brewster R. Q., *J. Amer. Chem. Soc.* **80**, 5861 (1958).
17. Dyson G. M., *J. Chem. Soc.* **1939**, 174.

Translated by Z. Votický