

SYNTHESIS, CHEMICAL PROPERTIES AND REACTIONS
OF HETERODIENES. I.SPECTRAL PROPERTIES OF PHENYL ISOSELENOCYANATES
AND THE POLAR CHARACTER OF THE NCSe GROUP

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The results of a study of infrared and ultraviolet spectra of a series of substituted phenyl isoselenocyanates are presented. A linear correlation between the $\nu_{\text{as}}(\text{NCSe})$ or the integrated intensities ($\log A$) and the Hammett's σ constants was found in the solvents of different polarity. An electron accepting character of the isoselenocyanate group was deduced from the correlation of $\nu_{\text{C=O}}$ of substituted acetophenones with the σ_{p} constants. Solvent effect investigation indicates a negative solvatochromy and a weak solvent-solute dipolar interaction. The structure and the polar character of the NCSe group is discussed.

In our previous papers we dealt with the syntheses, structure and reactivity of isothiocyanates exhibiting a remarkable biologic activity¹⁻³. Considering the close chemical relationship between selenium and sulphur, we become interested in the effect of the substitution of sulphur for selenium upon the chemical, physical, and biological properties of these compounds.

It follows from the discussion of the methods for the preparation of isoselenocyanates collected by Collard-Charon and Renson⁴ and by Bulka and coworkers that in spite of various possibilities of the preparation of substituted phenyl isoselenocyanates, the only method applied in practice is the addition of selenium to isonitriles. The isonitrile method is less suitable to the preparation of derivatives carrying strong electronaccepting substituents because of the decreased electron density on the end atom of the isonitrile group. The infrared spectra of isoselenocyanates are mentioned by Bulka and coworkers⁵, where is given a comparison of the fundamental frequencies of the NCSe and NCS groups. These authors found that the absorption maximum of the NCSe group is slightly shifted towards the higher frequencies with respect to isothiocyanates. The other maxima of this complex band are — in the contrary to the isothiocyanates — located at lower frequencies than the main maximum. The ultraviolet spectra of the isoselenocyanates have not been studied yet.

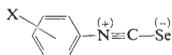
In this work, we tried to accumulate some new observations on the vibrational frequencies and the integrated intensities of the $\nu(\text{NCSe})$ vibration and the ultraviolet spectra of the phenyl isoselenocyanates in solvents of various polarity in order to get more detailed explanation of their structure and properties.

EXPERIMENTAL

Studied Compounds

4-Dimethylaminophenyl isothiocyanate, 4-methoxyphenyl isothiocyanate, 4-ethoxyphenyl isothiocyanate, 4-methylphenyl isothiocyanate, phenyl isothiocyanate, 4-chlorophenyl isothiocyanate, and 4-Acetylphenyl isothiocyanate were prepared according to the described methods⁶⁻⁸. The isoselenocyanates *I*–*VIII* were prepared by addition of selenium to the isonitriles⁹. The corresponding isonitriles were obtained by dehydration of the formanilides by POCl_3 in the presence of potassium tert-butoxide⁹. The following procedure was used: 0.1 mol of the isonitrile and 0.12 mol of Se suspended in 100 ml chloroform was refluxed 3 h under vigorous stirring. The reaction mixture is yellow at the beginning; later it gets a dark red colour. After completing the reaction, the excess of Se is filtered off and the chloroform is removed *in vacuo*. The crude product (73%) is recrystallized from a suitable solvent. The recrystallization causes large losses of the material but the product cannot be purified chromatographically because of the easy splitting of the selenium. The physico-chemical properties and the elemental analyses of the substituted phenyl isoselenocyanates are given in the Table I. The 4-substituted acetophenones were either of commercial origin or were prepared according to the literature¹⁰.

TABLE I
Prepared Phenyl Isoselenocyanates



Compound	X	Yield B. p., °C	Formulae (m. w.)	Calculated/Found		
				% C	% H	% N
<i>I</i>	4-CH ₃ CO	4.1	C ₉ H ₇ NOSe (224.1)	48.23	3.15	6.25
		108–109 ^a		48.22	3.13	6.23
<i>II</i>	4-Cl	24.6	C ₇ H ₄ ClNSe (216.5)	38.83	1.86	6.46
		70–71 ^a		38.79	1.91	6.40
<i>III</i>	H	25.3	C ₇ H ₅ NSe (182.1)	46.17	2.72	7.69
		70/3 ^b		46.20	2.74	7.62
<i>IV</i>	3-CH ₃	25.1	C ₈ H ₇ NSe (196.1)	48.99	3.59	7.14
		107–108/7 ^b		48.92	3.60	7.13
<i>V</i>	4-CH ₃	21.6	C ₈ H ₇ NSe (196.1)	48.99	3.59	7.14
		61.5–62 ^a		48.94	3.63	7.14
<i>VI</i>	4-C ₂ H ₅ O	26.1	C ₉ H ₉ NOSe (226.1)	47.80	4.01	6.19
		96–97 ^a		47.59	3.95	6.25
<i>VII</i>	4-CH ₃ O	23.7	C ₈ H ₇ NOSe (212.1)	45.30	3.32	6.60
		48–49 ^{b,c}		45.35	3.29	6.55
<i>VIII</i>	4-(CH ₃) ₂ N	17.7	H ₉ H ₁₀ N ₂ Se (225.2)	48.01	4.47	12.44
		100–101 ^a		48.06	4.38	12.38

^a Light petroleum, ^b b.p., °C/Torr, ^c benzene.

Spectral Measurements

The infrared absorption spectra in the region of $2300\text{--}1800\text{ cm}^{-1}$ were measured on a double-beam spectrophotometer Zeiss (Jena) model UR-20. The 0.05M solutions in cyclohexane, tetrachloromethane, chloroform, dimethylformamide, acetonitrile, and nitromethane were studied using NaCl cells (0.17 mm path length). The instrument was calibrated by a polystyrene foil. The integrated intensities of the absorption bands $\nu(\text{NCSe})$ were measured in tetrachloromethane and chloroform. The integration was performed by cutting an absorption band from the record (the plot of the extinction coefficient against the wavenumbers) and weighting the paper. The studied region was $2250\text{--}1900\text{ cm}^{-1}$. The concentration was varied in the range $0.02\text{--}0.07\text{M}$. The definition of the integrated intensity $A = 2.303 \int \epsilon dv$ was employed. The frequencies of the $\nu_{\text{C=O}}$ vibrations of acetophenones were determined at 1690 cm^{-1} in tetrachloromethane and chloroform (concentration 0.05M , NaCl cell, path length 0.26 mm). The ultraviolet absorption spectra of the studied compounds were measured on a registering spectrophotometer Perkin-Elmer 402 in the region of $210\text{--}400\text{ nm}$, in $3 \cdot 10^{-5}\text{M}$ methanolic solutions. The 4-methylphenyl isoselenocyanate and 4-methylphenyl isothiocyanate were also measured in n-hexane, cyclohexane, methanol ethanol, and acetonitrile.

RESULTS AND DISCUSSION

All studied isoselenocyanates exhibit a broad intense absorption band in the region of $2200\text{--}2000\text{ cm}^{-1}$, which can be (using the analogy of isothiocyanates) assigned to the $\nu_{\text{as}}(\text{NCSe})$ vibration. These absorption maxima are shifted towards the higher frequencies in comparison with the isothiocyanates (Fig. 1). We have found that the absorption bands due to $\nu_{\text{as}}(\text{NCSe})$ move towards the higher frequencies when increasing the polarity of the solvent. This effect indicates an increase of the force constant

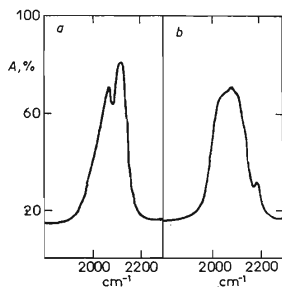


FIG. 1

Infrared Absorption Spectra of 4-Acetylphenyl Isoselenocyanate (a) and 4-Acetylphenyl Isothiocyanate (b) in Chloroform]

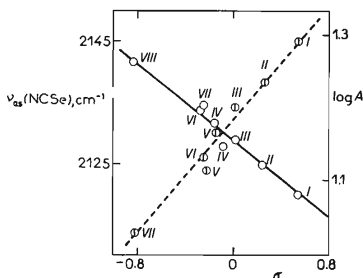


FIG. 2

Plot of $\nu_{\text{as}}(\text{NCSe})$ and $\log A$ of Isoselenocyanates I–VIII against Hammett's σ Values in Chloroform

and therefore also an increase of the bond order of the NCSe group (Table II). The reason is probably the mutual interaction of the acidic protons of the polar solvents with the non-bonding orbitals of the selenium atom that in turn increase the proportion of the limit resonance structure containing a triple bond in the ground state of the molecule.

Further we have investigated the effect of the substituents on the vibration frequencies of the NCSe group. We found a linear correlation between the vibration frequencies $\nu_{as}(\text{NCSe})$ and the Hammett's σ constants in all solvents used (Fig. 2). Solvent, ρ , r given: cyclohexane, -15.51 , 0.89 ; tetrachloromethane -16.69 , 0.92 ; chloroform, -16.14 , 0.89 ; dimethylformamide, -12.65 , 0.89 ; acetonitrile, -12.11 , 0.86 , nitromethane, -12.49 , 0.85 . For the comparison purposes we correlated the vibrational frequencies $\nu_{as}(\text{NCS})$ with σ constants in the chloroform solutions (Table II). The value

TABLE II
Spectral Properties of Substituted Phenyl Isoselenocyanates

Compound	$\nu_{as}(\text{NCSe})$ cm^{-1}						log A		λ_{max} , nm/log ϵ		σ^d	
	$\text{C}_6\text{H}_{12}^a$	CCl_4	CHCl_3^b		DMFA ^c	CH_3CN	CH_3NO_2	CCl_4	CHCl_3	1		2
I	2 110	2 114	2 120	(2 092)	2 126	2 131	2 132	1.2679	1.2883	312	250	0.502
										4.30	4.44	
II	2 111	2 115	2 125	(2 100)	2 132	2 135	2 136	1.2411	1.2358	297	238	0.227
										4.15	4.58	0.227
III	2 114	2 117	2 129	(2 110)	2 132	2 137	2 138	1.2135	1.2038	292	232	0.000
										4.09	4.63	
IV	2 111	2 120	2 128	—	2 131	2 132	2 134	—	—	292	232	-0.069
										3.92	4.33	
V	2 119	2 124	2 132	(2 118)	2 136	2 140	2 141	1.1881	1.1755	292	235	-0.170
										4.10	4.54	
VI	2 122	2 130	2 135	(2 120)	2 139	2 142	2 145	1.1735	1.1069	299	243	-0.240
										4.21	4.47	
VII	2 124	2 128	2 134	(2 120)	2 141	2 144	2 146	1.1909	1.1307	297	242	-0.268
										4.24	4.55	
VIII	2 128	2 133	2 141	(2 140)	2 142	2 146	2 147	1.1089	1.0338	324	308	-0.830
										4.52	4.46	

^a Solvents ordered according to the increasing E_T values¹⁶, ^b values in parentheses correspond to isothiocyanate, ^c dimethylformamide, ^d ref.¹⁵

of ρ_{NCSe} is markedly lower than the corresponding value for the isothiocyanates obtained in the same manner. That indicates that the isoselenocyanates are less susceptible to the substituent effects than their analogs ($\rho_{\text{NCS}} = -36.60$, $r_{\text{NCS}} = 0.99$). These results confirm the diminished ability of the mesomeric interaction of the NCSe group with the substituents on the aromatic ring. The integrated intensities of the absorption bands of the NCSe group ($\log A$) show a linear dependence upon the σ_p constants with a positive slope (chloroform, $\rho = 0.196$, $r = 0.981$; tetrachloromethane, $\rho = 0.119$, $r = 0.999$). By comparison of 4-chlorophenyl isothiocyanate and phenyl isothiocyanate¹¹ with their selenium analogs it becomes clear that the phenyl isoselenocyanates exhibit larger values of the integrated intensities (phenyl isocyanate has $\log A = 1.1673$ in CHCl_3 and 1.1848 in CCl_4 , 4-chlorophenyl isothiocyanate has $\log A = 1.2279$ both in CHCl_3 and CCl_4). Therefore, it can be concluded that the NCSe group of phenyl isoselenocyanates has a greater dipole than the NCS group. This fact is further confirmed by the study of the polar nature of the NCSe group. Since the synthesis of 4-carboxyphenyl isoselenocyanate failed and the appropriate value of the Hammett's constant could not be determined potentiometrically, we tried to estimate its value from the correlation of the σ constants of the *para*-substituents with the $\nu(\text{C}=\text{O})$ frequencies of the 4-substituted acetophenones. We have found (Fig. 3) a good correlation of these variables ($\rho = 17.18$, $r = 0.988$). The estimate of $\sigma_{p(\text{NCSe})} = +0.31 \pm 0.019$, $\sigma_{p(\text{NCS})} = +0.20 \pm 0.019$ (potentiometrically found value of $\sigma_{p(\text{NCS})}$ is $+0.38$ ref.¹²). Disregarding the limited accuracy of this method, it can be concluded that the NCSe group has a slightly greater electron accepting effect than the NCS group.

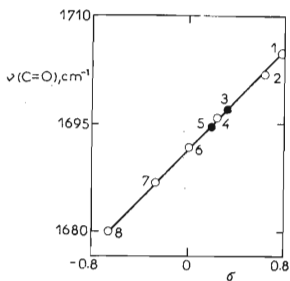


FIG. 3

Correlation of Vibration Frequencies $\nu(\text{C}=\text{O})$ of 4-Substituted Acetophenones with Hammett's σ_p Constants

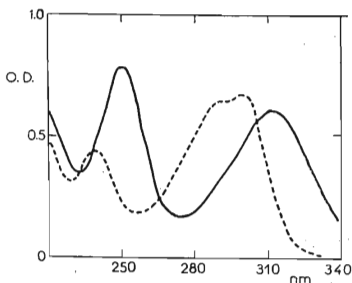


FIG. 4

Ultraviolet Absorption Spectra of 4-Acetylphenyl Isoselenocyanate (full line) and 4-Acetylphenyl Isothiocyanate (dashed line)

The values of λ_{\max} and $\log \epsilon$ of the ultraviolet absorption spectra of the isoselenocyanates are summarized in Table II. There are two characteristic absorption maxima at 300 and 230 nm in these spectra in the region of 220–300 nm. The UV spectra (Fig. 4) of isothiocyanates were studied in detail by Zahradník and coworkers^{13,14}, who have assigned the band at longer wavelength to the $V \leftarrow N(\pi - \pi^*)$ transition (corresponding to the p -band in the spectra of hydrocarbons) on the basis of quantum chemical calculations. This absorption band is in the case of isoselenocyanates shifted towards the longer wavelengths ($\Delta\lambda_{\max}$ 11–14 nm). The reason for the bathochromic effect of the isoselenocyanates lies probably in the different electro-negativity of sulphur and selenium atoms. From the Table II it further follows that only the substituents with markant mesomeric effect ($\pm M$) cause the bathochromic effect in the compounds *I*–*VIII*. This effect is not observed in the case of substituents with a weak mesomeric or inductive effect (due to the lower susceptibility of the studied conjugated system in comparison to the isothiocyanates).

TABLE III

Solvent Effect on the $\pi - \pi^*$ Absorption Band of 4-Methylphenyl Isoselenocyanate (λ_{\max} , E_{\max}) and 4-Methylphenyl Isothiocyanate (λ'_{\max} , E'_{\max})

Variable	n-Hexane	Cyclohexane	Acetonitrile	Ethanol	Methanol
E_1^{16}	30.9	31.2	46.0	51.9	55.5
λ_{\max} , nm	298	298	291	293	292
λ'_{\max} , nm	283	284	280	282	280
E_{\max} , kcal/mol	96.09	96.09	98.40	97.73	98.06
E'_{\max} , kcal/mol	101.18	100.82	102.26	101.54	102.26

We investigated also the solvent effect on the position of the first absorption band in the 4-methylphenyl isoselenocyanate and its thio-analog. In spite of the $\pi - \pi^*$ character of this band both compounds showed a negative solvatochromy (Table III). This behaviour can be explained by enhanced dipolar interaction of the polar solvents with the non-bonding orbitals of the selenium or sulphur atom, respectively, that causes hindering of the $p - \pi$ conjugation. The hypsochromic effect (n-hexane–methanol) amounts 6 nm (ΔE 1.97 kcal mol⁻¹) and 3 nm (ΔE 1.08 kcal mol⁻¹) for 4-methylphenyl isoselenocyanate and 4-methylphenyl isothiocyanate, respectively. Low values of the energy changes ΔE agree with the above stated rationalizations about the solvent–solute interaction (compare the results of the solvent effect in the IR spectra).

REFERENCES

1. Drobnička L., Zemanová M., Nemeč P., Antoř K., Kristián P., Martvoň A., Závodská E.: *Appl. Microbiol.* **16**, 582 (1968).
2. Augustín J., Drobnička L., Nemeč P., Antoř K., Kristián P., Martvoň A., Uher M.: *J. Antibiotics (Tokyo)* **21**, 504 (1968).
3. Horáková K., Drobnička L., Nemeč P., Kristián P., Antoř K., Martvoň A.: *Neoplasma* **16**, 3 (1969).
4. Charon C. C., Renson M.: *Bull. Soc. Chim. Belges* **71**, 531 (1952).
5. Bulka E., Ahlers K. D., Tuček E.: *Chem. Ber.* **100**, 1367 (1967).
6. Dyson G. M., George H. J., Hunter R. F.: *J. Chem. Soc.* **442**, (1927).
7. Dyson G. M., George H. J.: *J. Chem. Soc.* **125**, 1702 (1924).
8. Houben-Weyl: *Methoden der Organischen Chemie*, Vol. IX, p. 874. Thieme, Stuttgart 1955.
9. Ugi I., Meyr R.: *Chem. Ber.* **93**, 239 (1960).
10. Adams R., Noller C. R.: *Org. Syntheses, Coll. Vol. 1*, 109 (1946).
11. Kováč Š., Kristián P., Antoř K.: *This Journal* **30**, 3664 (1965).
12. Kristián P., Antoř K., Vlachová D., Zahradník R.: *This Journal* **28**, 1651 (1963).
13. Zahradník R., Vlachová D., Koutecký J.: *This Journal* **27**, 2337 (1962).
14. Svátek E., Zahradník R., Kjaer A.: *Acta Chem. Scand.* **13**, 442 (1959).
15. McDaniel D. H., Brown H. C.: *J. Org. Chem.* **23**, 420 (1958).
16. Reichardt C.: *Lösungsmittel-Effekte in der Organischen Chemie*, p. 142. Verlag Chemie, Weinheim 1969.

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