STUDY OF DIPOLE MOMENTS AND ELECTRON INTERACTIONS OF ISOSELENOCYANATES*

G.Suchár and P.Kristian

Department of Organic Chemistry,
P. J. Šafarik University, 041 67 Košice

The dipole moments of phenyl isoselenocyanates substituted in position 4 and of tert-butyl isoselenocyanate were measured in benzene solutions at 20°C. The structure and electron interaction of the NCSe group with electron donor and acceptor substituents are discussed on the basis of a comparison of the dipole moments with theoretical values calculated by vector analysis. The results are compared with those obtained with the corresponding sulphur and oxygen analogues.

Literature data about dipole moments of isoselenocyanates are lacking. Of the analogous derivatives, the dipole moments of phenyl isocyanates and phenyl isothiocyanates were reported in the literature[1,2]. With phenyl isoselenocyanates, we were interested mainly in the polar character of the NCSe group and its influence on the aromatic nucleus. This problem was dealt with also in our preceding work[3], where we discussed the structure and the polar character of the NCSe group on the basis of a correlation of spectral values with the Hammett substituent constants. Since the results from the spectral studies were not exhaustive, we turned our attention toward the study of electron effects of the isoselenocyanate group based on the dipole moments. The problem of the structure and spatial arrangement of isothiocyanates was studied in our previous work[4] based on the study of their dipole moments. The results indicated the C—N—C angle to be close to 180° and the mesomeric interaction of this group to be very small.

The present work concerns the study of the dipole moments of isoselenocyanates to elucidate the structure, spatial arrangement and electron interactions of the NCSe group.

EXPERIMENTAL

Chemicals

Phenyl isoselenocyanate *(I)*, m.p. 70°C at 3 Torr, 4-chlorophenyl isoselenocyanate *(II)*, m.p. 70—71°C, 4-methylphenyl isoselenocyanate *(III)*, m.p. 61·5—62°C, 4-ethoxyphenyl isoselenocyanate *(IV)*, m.p. 96—97°C, 4-methoxyphenyl isoselenocyanate *(V)*, m.p. 48—49°C, 4-dimethylaminophenyl isoselenocyanate *(VI)*, m.p. 100—101°C, and 4-acetylphenyl isoselenocyanate *(VII)*,

---

TABLE I

Values of Polarization (in cm^3) and Dipole Moments (in D) of Isoselenocyanates in Benzene at 20°C ^{a}

No	$N_2 \cdot 10^3$	ε	n^{20}	d_{20}	∞P_2 R_D	$\mu(0\%)$ (5%) (15%)	μ_{calc} μ_1
I	0·00	2·2766	1·5009	0·8782	290·9	3·41	—
	1·89	2·3158	1·5014	0·8796	48·4	3·39	
	4·99	2·3623	1·5023	0·8821		3·36	
	8·32	2·4099	1·5031	0·8845			
II	0·00	2·2814	1·5010	0·8779	140·6	2·04	—
	2·01	2·2847	1·5016	0·8802	54·1	2·00	
	5·30	2·3174	1·5026	0·8842		1·94	
	8·12	2·3255	1·5036	0·8870			
III	0·00	2·2758	1·5010	0·8779	373·3	3·91	3·63
	2·25	2·3239	1·5016	0·8800	54·8	3·89	+0·26
	5·04	2·3857	1·5023	0·8820		3·86	
	8·09	2·4559	1·5032	0·8846			
IV	0·00	2·2713	1·5010	0·8779	484·5	4·51	—
	2·02	2·3385	1·5016	0·8799	61·3	4·49	—
	5·04	2·4316	1·5026	0·8825		4·46	
	2·08	2·5196	1·5035	0·8856			
V	0·00	2·2816	1·5012	0·8785	432·6	4·25	3·94
	2·01	2·3309	1·5018	0·8807	57·0	4·23	+0·31
	5·34	2·4198	1·5029	0·8837		4·20	
	8·13	2·4994	1·5038	0·8866			
VI	0·00	2·2772	1·5010	0·8782	772·0	5·81	4·7
	2·00	2·3841	1·5018	0·8799	68·6	5·80	+1·14
	5·14	2·5396	1·5033	0·8828		5·77	
	8·12	2·6863	1·5047	0·8856			
VII	0·00	2·2780	1·5009	0·8782	—	2·38	2·72
	1·70	2·2953	1·5015	—	—	—	—0·18
	3·06	2·3066	1·5021	—			
	4·27	2·3190	1·5025	—			
VIII	0·00	2·2777	1·5011	0·8786	388·7	4·06	—
	2·04	2·3318	1·5012	0·8793	45·1	4·05	—
	5·20	2·4041	1·5013	0·8805		4·02	
	7·94	2·4719	1·5014	0·8815			

^{a} N$_2$ Mole fraction, ε dielectric constant, n_{20}^D refractive index, d_{20} density.

m.p. 108—109°C, were described in our preceding work[3]. Tert-butyl isoselenocyanate (*VIII*), m.p. 51·5—52°C, was synthesized according to the literature[5]. The solvent was UV-spectrally pure benzene dried by contact with metallic sodium and distilled on a column (b.p. 80·1°C at 760 Torr). It was stored over a molecular sieve of the type "Nalsit-4" and was allowed to flow prior to use through a column filled with activated alumina.

Dipole Moments

Measurements of the dielectric constant, ε, were carried out on a DM 01 type dipole meter (Wissenschaftlich-technische Werkstätten, G.m.b.H.) with an accuracy to within ± 0.0001. We used a tempered dielectric cuvette of the type DFL 2, the volume of the measured solution being 4 ml. The measurements were performed at four concentrations ranging from 0·015 to 0·08M at 20°C and at a frequency of 2·0 MHz. The densities were determined in 10 ml pycnometers for volatile compounds. The refractive indexes were measured on an Abbe immersion refractometer. The values of the dipole moments were calculated according to Halverstadt and Kumler[6] with a correction for atomic polarization. In the case of 4-acetylphenyl isoselenocyanate, the value of μ was determined according to Guggenheim[7]. The following literature data were made use of in the calculations: Bonding moments (in Debye units): H—C_{ar} 0·0; C—N 0·45; C_{ar}—NO_2 4·0; C_{ar}—Cl 1·6; C=N 1·8; C≡N 3·6; C—O 0·74; C=O 2·5; C—S 0·9; C=S 2·6 (ref.[8]); C—Se 0·70 (ref.[9]). Group moments (in Debye units) and their angles (in parentheses, degrees): Ar—CH_3 0·37 (0); Ar—OCH_3 1·28 (72); Ar—$COCH_3$ 2·96 (48) (ref.[9]); Ar—$N(CH_3)_2$ 1·58 (34) (ref.[10]). Dipole moments of the following compounds (in Debye units): Phenyl isocyanate 2·28; ethyl isocyanate 2·81; 4-chlorophenyl isocyanate 0·84 (ref.[2]); phenyl isothiocyanate 2·91; 4-chlorophenyl isothiocyanate 1·51; 4-methylphenyl isothiocyanate 3·3; 4-nitrophenyl isothiocyanate 1·23; tert-butyl isothiocyanate 3·73 (ref.[4]). Bond lengths (in Å units): C=N 1·28; C≡N 1·16; C—O 1·34; C—S 1·75 (ref.[11]); C—Se 1·97 (ref.[12]).

RESULTS AND DISCUSSION

The measured and calculated dipole moment values for the studied compounds are summarized in Table I. It follows from the dipole moments of the phenyl isoselenocyanates *I*—*VII* that the NCSe group has a strongly polar character with an electron-acceptor effect on the aromatic nucleus. It is interesting that in spite of the smaller electronegativity of selenum as compared with sulphur and oxygen the dipole moments increase in the order $\mu_{NCO} < \mu_{NCS} < \mu_{NCSe}$ (Table II). The reason for this can be seen in the effect of several factors. For example, changes in the atomic radius cause changes in the bond lengths and so also in the bond moments of the groups C=X (X = Se, S, O). The change in the character of the end double bond (C=X) of the mentioned heterocumulenes caused by a lowered π-bond interaction between the $2p\pi$, $3p\pi$ and $4p\pi$ orbitals of the hetero atom and the $2p\pi$ orbital of the carbon atom effectuates also a change in the polarity of these bonds (unwillingness of the S or Se atoms to form a double bond). The mentioned differences cause also a different role of the mesomeric structures. Changes in the dipole moments of the heterocumulenes can be also related to different mesomeric interactions between the mentioned heterocumulene systems and the aromatic nucleus. To elucidate this question,

it was necessary first to determine the geometry of the corresponding groups. In the case of isothiocyanates, certain results of X-ray analyses and microwave spectra were available. With isothiocyanates for which no mesomeric interaction is possible, angles of about 140° or less were measured, *e.g.*, 142° for CH_3NCS and 130° for HNCS and DNCS[13,14]. The bond angle for 4-bromophenyl isothiocyanate was determined by X-ray analysis[15] as 155°.

For the calculation of the C—N—C angle of the NCS group in phenyl isothiocyanates, we used the graphical method according to Woerden and Having[16] on the basis of the dipole moments of phenyl, 4-chlorophenyl, 4-nitrophenyl, and 4-methylphenyl isothiocyanates. (The NCS group moment was determined as $\mu_{NCS} = 2\cdot91$ D; $\Theta = 20°$.) From these values and from the C—N bond moment, $0\cdot45$ D, we determined the C—N—C bond angle as 164°. With regard to the fact that for the analogous isocyanates and isoselenocyanates no dipole moment values of suitable compounds were available to enable using the mentioned method, we attempted to calculate these values with the aid of only one substituent, 4-Cl (*II, IX, X*, Table II). With isothiocyanates, it is seen that there is a good agreement between the values obtained by both these methods (C—N—C angle: 164°, 159°).

TABLE II
Experimental Values of Dipole Moments (in D) and Calculated C—N—C Bond Angles for Heterocumulenes $4\text{-ClC}_6\text{H}_4\text{N}{=}\text{C}{=}\text{X}$

No	X	$\mu_{exp.}$	μ_{Ar-NCX}	Θ^0	$\sphericalangle$ C—N—C
II	Se	2·04	3·41	23	154
IX	S	1·51	2·91	18	159
X	O	0·84	2·28	14	163

TABLE III
Calculated Dipole Moments (in D) of Extreme Mesomeric Structures

X	—N=C=X (*A*)	$\overset{(+)}{-\text{N}}{=}\text{C}\overset{(-)}{-\text{X}}$ (*B*)	$\overset{(+)}{-\text{N}}{=}\text{C}\overset{(-)}{-\text{X}}$ (*C*)
O	1·00	9·59	5·80
S	1·06	11·72	7·90
Se	—	12·57	8·80

The dipole moments of the mesomeric structures of the NCSe, NCS and NCO groups bound to the aromatic nucleus (Table III) were calculated graphically by vector addition of the bond moments. To this purpose the C—N—C bond angles indicated in Table II were used. The dipole moment for the nonpolar structure NCSe (A) is not indicated in Table III since the C=Se bond moment has not been known. Based on an analogy with the corresponding oxygen and sulphur derivatives, the value of $\mu_A \approx 1$ can be expected for the Se derivative. From the comparison of the experimental dipole moment values of the mentioned derivatives with the calculated moments of the mesomeric structures it follows that the mesomeric structure B contributes only to an insignificant extent to the real structure of the studied hetero-cumulenes, which can be best expressed by the mesomeric structures A and C (Table III).

Further we attempted to estimate the mesomeric interaction of the studied hetero-cumulenes from the differences between the dipole moments of the corresponding aromatic and aliphatic compounds (Table IV). The mesomeric moments μ_M indicate that the mesomeric effect of the NCX groups increases in the order NCO < NCSe < < NCS. In our opinion, this order is related to the magnitude of the positive charge on the C atom in the mentioned groups, *i.e.*, the larger will be the electron deffect on the central C atom of the heterocumulenes, the less easily will be the interaction between the π-bond systems of functional groups of NCX and aromatic nucleus. In accord with this statement are the reactivities of these compounds in nucleophilic addition reactions; they increase in the order[17] NCS < NCSe < NCO. Hence, there is an indirect relation between the mesomeric interaction and reactivity of these groups.

To obtain an idea about the mutual interaction of the NCSe groups with the electron-acceptor and electron-donor substituents, we calculated the interaction moments μ_i as the vector difference of experimental and calculated dipole moments

TABLE IV

Experimental Dipole Moments (in D) for Aromatic and Aliphatic Isoselenocyanates, Isothio-cyanates, and Isocyanates, and Mesomeric Moment μ_M

X	C_6H_5—X	$(CH_3)_3C$—X	C_2H_5—X	μ_M
NCO	2·28	—	2·81	—0·53
NCS	2·91	3·73	3·64	—0·82[a]
NCSe	3·41	4·06	—	—0·66

[a] —0·73 D.

of phenyl isoselenocyanates substituted in position 4 (Table I). With respect to the assumed +M effect of the NCSe group (Table IV) we expected a pronounced mesomeric interaction mainly in the case of electron-acceptor substituents. However, it turned out the interaction moments are much higher in the case of electron-donor substituents (Table I). This fact can be attributed to the strong electron-acceptor character of the NCSe group, which can accordingly interact with the electron-donor substituents by means of the π-electron inductive effect. On the other hand, the relatively low value of μ_i for 4-acetophenyl isoselenocyanate (VII, -0.18 D) reveals a weak $p - \pi$ electron interaction of the NCSe group with the electron-acceptor substituents. Our results are in accord with the known concept about the structure and electron character of heterocumulenes of the type $N=C=X$ ($X = $ Se, S, O).

REFERENCES

1. Landolt-Börnstein: *Zahlenwerte und Funktionen,* Vol 1/3. Springer, Berlin 1951.
2. Osipov O. A., Minkin V. I.: *Spravochnik po Dipolnym Momentam.* Vysshaya Shkola, Moscow 1965.
3. Kristian P., Suchár G.: This Journal *37,* 3066 (1972).
4. Antoš K., Martvoň A., Kristian P.: This Journal *31,* 3737 (1966).
5. Jensen K. A., Felbert G., Pedersen C. Th., Svanholm U.: Acta Chim. Scand. *20,* 278 (1966).
6. Halverstadt I. F., Kumler W. D.: J. Amer. Chem. Soc. *64,* 2988 (1942).
7. Guggenheim E. A.: Trans. Faraday Soc. *45,* 714 (1949).
8. Exner O.: Chem. listy *60,* 1047 (1966).
9. Minkin V. I., Osipov O. A., Zhdanov J. A.: *Dipolnye Momenty v Organicheskoi Khimii.* Khimia, Moscow 1968.
10. Hepworth J. D., Hudson J. A., Ibbitson D. A., Hallas G.: J. Chem. Soc., Perkin Trans. 2, 1905 (1972).
11. March J.: *Advanced Organic Chemistry: Reactions, Mechanism and Structure,* p. 22. McGraw-Hill, New York 1958.
12. *Spravochnik Khimika,* Vol. I, p. 364. Goskhim. Izd., Moscow 1963.
13. Beard C. I., Dailey B. I.: J. Amer. Chem. Soc. *71,* 929 (1949).
14. Zeiger H. J.: J. Chem. Phys. *21,* 416 (1953).
15. Ulický L.: Sb. Pr. Chemickotechnol. Fak. SVŠT, Bratislava *1971,* 47.
16. Woerden H. F., Having E.: Rec. Trav. Chim. *86,* 341 (1967).
17. Kristian P., Suchár G., Podhradský D.: This Journal *40,* 2838 (1975).

Translated by K. Micka.