DIPOLE MOMENTS AND STRUCTURE OF ORGANOSELENIUM COMPOUNDS

VI. ALLYLPHENYLSELENIDE AND SOME OF ITS DERIVATIVES

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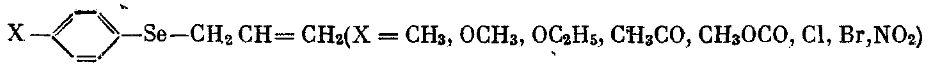
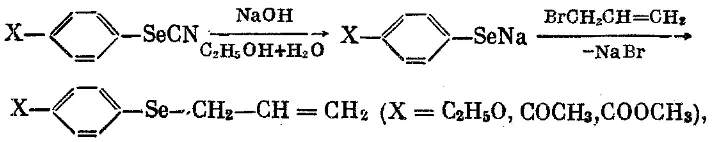
This communication presents the results of an investigation of the structure of molecules according to the method of dipole moments of allylphenylselenide, first produced in 1966 [1], its derivatives

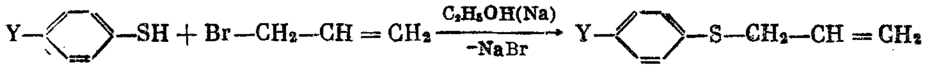

$(X = CH_3, OCH_3, OC_2H_5, CH_3CO, CH_3OCO, Cl, Br, NO_2)$

and certain sulfides of analogous structure. Part of the investigated compounds were described earlier [1, 2]. For the remainder, the physical properties and data of analysis are cited in Table 1.

The selenides were produced by condensation of the corresponding arylselenocyanates with allyl bromide:

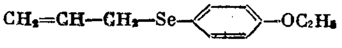
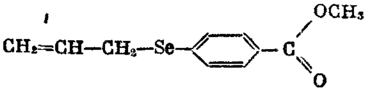
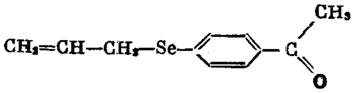
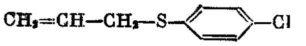
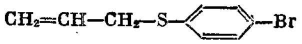
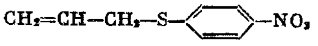

$(X = C_2H_5O, COCH_3, COOCH_3)$,

while the sulfides were produced by condensation of allyl bromide with aromatic thiols, analogously to [2]:


$(Y = Cl, Br, NO_2)$

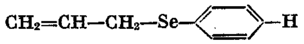
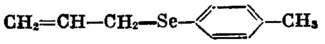
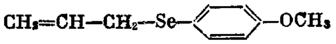
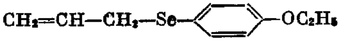
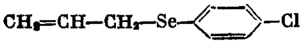
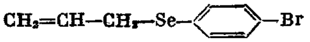
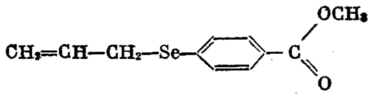
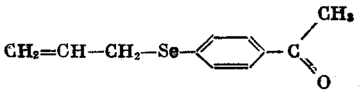
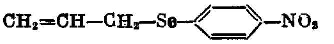
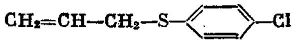
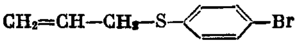
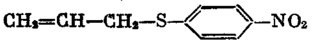
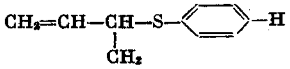
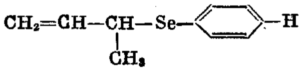
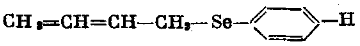
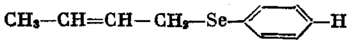
The dipole moments were measured in benzene solutions at 25°, analogously to [3].

TABLE 1. Physical Properties of Substances and Data of Analysis

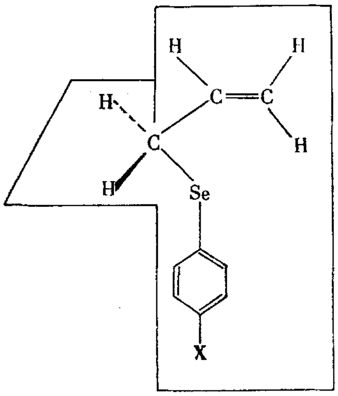
Substance	Bp, deg/mm (mp)	n_D^{25}	d_4^{25}	Found, %		Calc., %	
				C	H	C	H
	135°/7	1,5778	1,2666	54,69	5,79	54,78	5,85
	(90—91°)			51,65	4,71	51,78	4,74
	(46—47,5°)			55,33	5,21	55,24	5,06
	123°/14	1,5819	1,1543	58,28	5,02	58,53	4,91
	138°/13	1,6065	1,4048	47,09	4,02	47,17	3,96
	(37,5—38°)			55,66	4,60	55,37	4,64

V. I. Ul'yanov-Lenin Kazan' State University. Translated from Zhurnal Strukturnoi Khimii, Vol. 12, No. 1, pp. 179-182, January-February, 1971. Original article submitted January 3, 1970.

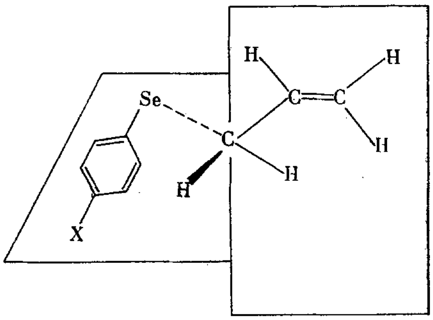
TABLE 2. Calculated and Experimentally Measured Dipole Moments (D)

Substance	Type of structure			μ_{meas}
	I	II	III	
1. 	1,56	1,43	1,52	1,39
2. 	1,82	1,73	1,76	1,53
3. 	2,14	2,08	1,89	2,10
4. 	2,14	2,08	1,89	2,03
5. 	1,44	1,56	1,45	1,58
6. 	1,42	1,53	1,43	1,36
7. 	1,85	1,81	1,11	1,44
8. 	2,35	2,42	1,68	2,75
9. 	4,02	4,18	4,04	4,25
10. 	1,57	1,66	1,50	1,75
11. 	1,55	1,64	1,46	1,68
12. 	4,35	4,29	3,95	4,43
13. 	1,70	1,50	1,62	1,69
14. 	1,56	1,43	1,52	1,48
15. 	1,51	1,45	1,46	1,51
16. 	1,65	1,55	1,61	1,57

For the molecules of the substances investigated $X-C_6H_4-Se-CH_2-CH=CH_2$, two basic types of structures are possible (without considering variations with internal rotation), differing in whether the phenylseleno (or phenylthio) group and ethylenic bond are situated in the same plane or in two mutually perpendicular planes.

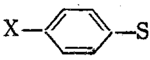


I



II

For each of these two types of structures, several variations are possible, determined by rotation of the substituted phenylseleno (phenylthio) group around the C−Se (or, correspondingly, C−S) bond, as well as on account of different arrangement of irregular substituents in the para position of the benzene ring. The dipole moments of various variations of the structures of the first and second type were calculated according to the moments of the bonds and groups indicated in [4-6], considering the valence angles of CSeC 106° and CSC 109° [7]. The addition of two vectors in mutually perpendicular planes was performed using the ratio $\cos \gamma = \cos \alpha \cos \beta$, permitting a determination of the angle γ between the vectors according to the values of α and β, each of which is the angle between one of the component vectors and the lines of intersection of the planes.

When the dipole moments of substances 5, 6, 9-12 were calculated according to an additive scheme (Table 2), we used the experimental values of the dipole moments of the compounds X——Se(S)—CH_3 [8], according to which we determined the moment of the fragment X ——Se(S).

Without going into a consideration of the fine details of structure and considering that certain rotational isomers have the same dipole moment, we have cited in Table 2 the calculated values of the dipole moments only for one variation of each type of structures I and II. For compounds with irregular substituents X, each of the values cited is an average between two, pertaining to different cases of arrangement of the vector of the dipole moment of the irregular group in the plane of the benzene ring. The third type of structure (III), for which the calculated values of the dipole moment are cited in Table 2, differs from structure II by free rotation of the $X-C_6H_4-Se(S)$ group around the Se(S)−C bond (the calculation was performed according to the formula indicated in [5]). Rotation of the ethylene group around the $C_{sp^2}-C_{sp^3}$ bond has no effect on the value of the dipole moment of the molecule.

From the data of Table 2 it is evident that different variations of the structure of the allylphenylselenide, α- and γ-methylallylselenide, and p-phenyleneallylselenide molecules in the corresponding thio analogs are characterized by close values of μ_{calc}, since it is difficult to select between them according to the method of dipole moments, although the calculated values of the dipole moments coincide rather well with the experimental values.

LITERATURE CITED

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8. O. A. Osipov and V. I. Minkin, Handbook of Dipole Moments [in Russian], Vysshaya Shkola, Moscow (1965).