

DIPOLE MOMENTS AND STRUCTURE OF SOME ORGANOSELENIUM COMPOUNDS

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SUMMARY

The dipole moments of di-*p*-tolyl selenide (1.74 D), di-*o*-tolyl selenide (1.00 D), di-*m*-tolyl selenide (1.65 D), di-*p*-anisyl selenide (2.35 D) and di-*p*-tolyl selenium dichloride (3.69 D) have been determined in benzene at 35°. The results are analysed in terms of mesomeric effects and internal rotation in these systems. The dipole moments of a few aliphatic selenides have been theoretically evaluated.

INTRODUCTION

From the point of view of physical measurements in relation to structure, organoselenium compounds have not received as much attention as the analogous sulphur and oxygen compounds^{1,2}. This is especially the case with regard to dipole moment measurements³. It is to be expected from electronegativity considerations that the mesomeric effect of the heteroatoms attached to the benzene ring will vary in the order O > S > Se². An analysis of the dipole moments of several aliphatic and aromatic selenides should throw much light on this point^{3,4}. Consequently the dipole moments of a few aromatic selenides have been measured in benzene solution at 35°. For comparison, the dipole moments of aliphatic selenides have been calculated from the charge distribution scheme of Smith, Ree, Magee and Eyring⁵.

EXPERIMENTAL

Materials

Di-*o*-, *m*- and *p*-tolyl selenides and di-*p*-tolyl selenium dichloride were all prepared by the method of Leicester and Bergstrom^{6,7}. Both *o*- and *p*-tolyl selenides were repeatedly recrystallised from alcohol while di-*p*-tolyl selenium dichloride was crystallised from benzene. The melting points agreed with the literature values^{7,8}. Di-*m*-tolyl selenide, a liquid at room temperature, was distilled under reduced pressure (192–195°/20 mm). Di-*p*-anisyl selenide was prepared by the method of Boyd *et al.*⁹, and was repeatedly recrystallised from 95% ethanol; m.p. 57° (lit. 56.5–58°).

Benzene used for dielectric measurements was purified as described in the literature¹⁰; ϵ^{35} 2.2535 and d^{35} 0.86278.

Apparatus and methods of measurements

The dielectric constant measurements were made with an a.c. mains operated heterodyne beat apparatus as described earlier¹¹. Densities of the solutions were obtained using an Ostwald-Sprengel Pyknometer with ground-in caps at both ends. The polarisation of the solute at infinite dilution was obtained using the mean values of Hedestrand constants α and β ¹². Electronic polarisation of the solute was calculated by addition of bond refraction values¹³. Atomic polarisation was taken as 5% of the electronic polarisation. Tables 1 and 2 summarise the results of the measurements.

TABLE 1

DIELECTRIC CONSTANT AND DENSITY DATA IN BENZENE AT $35 \pm 0.02^\circ$

$f_2 \times 10^4$	Dielectric constant (ϵ)	Density d	$f_2 \times 10^4$	Dielectric constant (ϵ)	Density d
<i>p</i> -Tolyl selenide			<i>p</i> -Anisyl selenide		
0.000	2.25420	0.862775	0.000	2.25680	0.862800
8.74 ₄	2.25845	0.863524	14.11	2.26838	0.864546
23.12	2.26548	0.864777	23.82	2.27658	0.865672
34.04	2.27158	0.865929	34.60	2.28760	0.867152
44.87	2.27620	0.866925	31.56	2.28381	0.866705
58.10	2.28397	0.868186	49.20	2.29758	0.868859
<i>m</i> -Tolyl selenide			<i>p</i> -Tolylselenium dichloride		
0.000	2.25190	0.862440	0.000	2.25400	0.862750
27.53	2.26475	0.865184	5.66 ₉	2.26499	0.863765
36.67	2.26952	0.866080	7.55 ₉	2.26844	0.863949
48.83	2.27530	0.867376	10.08	2.27369	0.864344
<i>o</i> -Tolyl Senenide			13.42	2.28241	0.864873
0.000	2.25262	0.862800			
8.66 ₃	2.25470	0.863642			
17.67	2.25695	0.864505			
23.92	2.25845	0.865135			
32.66	2.26062	0.866031			

TABLE 2

POLARISATION DATA FOR SELENIUM COMPOUNDS

Compound	Hedestrand's α	Hedestrand's β	P_T	P_E	P_0^*	μ in Debyes
<i>p</i> -Tolyl selenide	2.2064	1.0571	135.68	72.60 ^a	59.45	1.7 ₄
<i>o</i> -Tolyl selenide	1.0808	1.1307	95.59	72.60 ^a	19.36	1.00
<i>m</i> -Tolyl selenide	2.1139	1.1596	129.79	72.60 ^a	53.56	1.65
<i>p</i> -Anisyl selenide	3.7186	1.4302	187.89	75.3 ^b	108.83	2.35
<i>p</i> -Tolylselenium dichloride	8.5807	1.8350	354.79	81.6 ^c	269.11	3.69

^a From reference 3. ^b Estimated from the empirical constants of Eisenlohr²⁰ along with the value 12.6 for Se and 26.21 for benzene³. ^c Estimated from the experimental MR_D value of 74 for $(C_6H_5)_2SeCl_2$ ¹⁹. * P_A is taken as equal to 5% P_E .

Calculations based on the Smith et al.⁵ method

On the charge distribution scheme of Smith *et al.*, each bond is uniquely characterised by two parameters, but the effective moment of each depends on the whole molecule. One of the parameters β is derived from bond polarisabilities. The other parameter γ (or α) is obtained from dipole moment data for a basic molecule. Bond angles and bond distances are taken from Sutton's table of interatomic distances²⁵. The results of the calculation are summarised in Tables 3, 4 and 5.

TABLE 3

PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION

Bond (a-b)	β_{ab}	γ_{ab}	Ref.
H-C	0.13	0.00	
H-Se	0.0668	0.132	^a
Se-C	$\beta_{Se}^{Sc} = 0.441$ $\beta_C^{Sc} = 1.016$	$\alpha_{C-Se} = 1.293$	^b
C-C	$\beta_C^{Cc} = 0.718$	$\alpha_{CC} = 0$	

^a γ_{H-Se} was derived from the moment of 0.24 D for hydrogen selenide²¹. β_{H-Se} was derived from the bond refractivity value of 6.34 cc for the Se-H bond calculated from the data of Tschugaeff²², using tabulated bond refractivities¹³. ^b Both β_{Se}^{Sc} and β_C^{Sc} were calculated using the bond refractivity value of 6.03 cc for Se-C bond calculated from the data of Tschugaeff²². α_{C-Se} was derived from the dipole moment value of 1.32 D for dimethyl selenide⁴.

DISCUSSION

An X-ray structure analysis of *p*-tolyl selenide¹⁴ shows that the C-Se-C angle is 106°. Using this value and the dipole moment of diphenyl selenide recalculated by Lumbroso⁴ (1.50 D) from the data of Bergmann *et al.*¹⁵ and taking the bond moments³ H-C=0.4 D and C_{aliphatic}-C_{aromatic}=0.4 D, the C_{aromatic}-Se bond moment is obtained as 0.85 D. The moment calculated for di-*p*-tolyl selenide is then 1.86 D, in close agreement with the experimental value (Table 2).

For di-*o*-tolyl and di-*m*-tolyl selenides three extreme configurations are possible: Ia, Ib and Ic and IIa, IIb and IIc respectively.

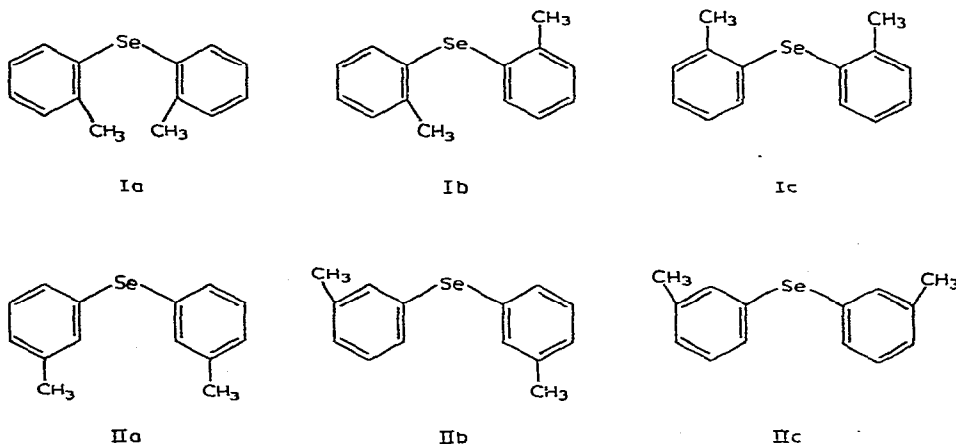


TABLE 4

CHARGE DISTRIBUTION IN SELENIUM COMPOUNDS

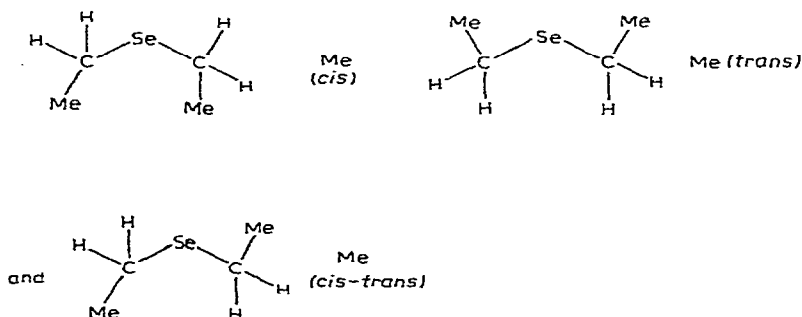
Compound	Carbon-1	Carbon-2	Hydrogen-1	Hydrogen-2	Selenium	Hydrogen attached to Se
CH ₃ SeH	0.415	—	0.054	—	-0.665	0.088
(CH ₃) ₃ C-SeH	0.279	0.095	—	0.012	-0.757	0.081
(CH ₃) ₂ Se	0.356	—	0.046	—	-0.989	—
(CH ₃ -CH ₂) ₂ Se	0.302	0.103	0.039	0.013	-1.048	—
[(CH ₃) ₃ C] ₂ Se	0.232	0.079	—	0.010	-1.123	—

TABLE 5

COMPARISON OF OBSERVED AND CALCULATED DIPOLE MOMENTS

Compound	$\mu_{\text{experimental}}$ (D)	$\mu_{\text{calculated}}$ (D)
CH ₃ SeH	^a	1.22
(CH ₃) ₃ C-SeH	^a	1.46
(CH ₃) ₂ Se	1.32 ^b	—
(CH ₃ -CH ₂) ₂ Se	1.52 ^b	1.80, 1.21, 1.50 ^c
[(CH ₃) ₃ C] ₂ Se	^a	1.69

^a Experimental values not available. ^b Values taken from McClellan's Tables²³. ^c The three calculated values are for the structures

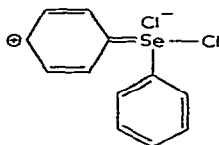


The moments calculated for structures Ia, Ib and Ic are 1.74, 1.37 and 0.91 D respectively, while those for structures IIa, IIb and IIc are 2.10, 1.72 and 1.27 D respectively. The experimental moments for *o*-tolyl and *p*-tolyl selenides are 1.00 and 1.65 D respectively. The values of dipole moments of di-*o*-tolyl and di-*m*-tolyl selenides assuming equal probability of all configurations turn out to be 1.38 and 1.73 D respectively. Thus in the case of *m*-tolyl selenide there is complete free rotation about the single bonds. In the case of *o*-tolyl selenide the experimental moment is significantly lower than that calculated assuming free rotation, indicating that the contribution of structures Ia and Ib, which are more polar than Ic should be less than that of structure Ic. From steric considerations structure Ic should be the most favourable one, since in structures Ia and Ib there is considerable repulsive interaction between the two Me groups or the Me group and the hydrogen on the *ortho*-carbon atoms.

The preponderance of structure Ic is reflected in the fact that the experimental moment is closer to the value calculated for structure Ic than for structures Ia and Ib.

In calculating the dipole moment of *p*-anisyl selenide, the bond moment of $C_{\text{aromatic}}-\text{OCH}_3$ is taken as 1.37 acting at an angle of 119° to the benzene ring as derived by Rogers¹⁶. Using this value, and assuming free rotation, the dipole moment of *p*-anisyl selenide turns out to be 2.49 in close agreement with the experimental value (Table 2). The results thus indicate that there is no significant mesomeric interaction between the lone pairs on the selenium and the methoxy groups.

An X-ray investigation of the diphenyl selenium dichloride¹⁷ and di-*p*-tolylselenium dihalides¹⁸ shows a slightly distorted trigonal bipyramidal structure with a Se atom at the center, the halogen atoms at the apices and the two aryl groups plus an unshared electron pair in the equatorial positions. The large moment found for diphenylselenium dichloride in benzene solution may be satisfactorily accounted for in terms of the above structure, if contributions from resonating polar forms such as:



are taken into consideration^{17,19}. In the present investigation the dipole moment of di-*p*-tolylselenium dichloride is found to be 3.72 D. The higher value for di-*p*-tolylselenium dichloride compared with diphenylselenium dichloride arises from the contribution of 0.4 D by the Me group towards the moment. The increase in moment due to methyl substitution in the diaryl Se dichloride is of the same order as that found in the simple diaryl selenides.

The dipole moments of a few aliphatic selenides have been evaluated using the method of Smith *et al.*⁵ (Table 5). The observed dipole moment of diethyl selenide can best be accounted for on the basis of a structure in which the two Me groups are in *cis-trans* position with respect to each other (Structure shown in the footnote to Table 5). Calculated values of dipole moments of a few other aliphatic selenides are also shown in Table 5, but experimental data for these compounds are not available.

The mesomeric moments operating in the system PhXH where X = O, S and Se is derived as the difference between the experimentally observed value for PhXH and that calculated for MeXH using charge distribution scheme of Smith *et al.*

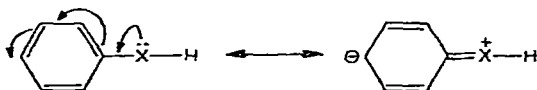
TABLE 6

MESOMERIC MOMENTS IN THE SYSTEM PhXH (X = O, S OR Se)

Compound	Exptl. moment PhXH (μ_1) ^a	Calculated value for MeXH (μ_2) ^b	Mesomeric moment $\mu_1 - \mu_2$
PhOH	1.40	1.61	-0.21
PhSH	1.30	1.36 ^c	-0.06
PhSeH	1.10	1.20	-0.10

^a Values taken from ref. 23. ^b Calculated using the method of Smith *et al.* (see text). ^c Taken from ref. 24.

(Table 6). The extent of mesomerism decreases in the series $O > S \geq Se$. The direction of the mesomeric moment is explicable in terms of contribution of structures such as:



This procedure of assuming the extent of mesomerism is not, however, applicable to diaryl compounds Ar_2X because the parameters employed in the calculations have themselves been derived from the experimental dipole moments of Me_2X .

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