DIPOLE MOMENTS AND CONFORMATION
OF SOME ORGANIC SELENIUM COMPOUNDS

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Dipole moments of diselenides *I*, *II* and four selenoesters *III*— *VI*, altogether compounds of the aromatic series, have been measured in benzene solution. From the results, their conformations have been established by a comparison with the *para*-derivative and the previously described graphical method. All the molecules studied possess essentially the same conformation as the corresponding sulfur and oxygen analogues.

One important aspect of selenium chemistry is a comparison with the corresponding sulfur and oxygen derivatives. In general, there is less difference among the heavier atoms than between the first-row and second-row elements, the main reason being attributed to the participation of *d*-electrons. As far as the conformation is concerned, the main variable factors in the sequence O, S, Se, and Te are the increasing covalent radius resulting in lowering the rotational barrier around single bonds[1], the decreasing valency angle due to changes of hybridization[2], and decreasing conjugation due to less effective $3p - 2p$ overlap compared with $2p - 2p$. In addition, these factors change more from O to S than among the heavier atoms[1]. It is also not surprising that the few studies devoted to the conformation of selenium compounds revealed essentially the same conformation as found in the corresponding sulfur derivatives[3–9]. These papers dealt with the conformation of the Se—Se bond of diselenides[3–7].

Continuing our previous studies on O-alkyl[10] and S-alkyl[11] thiocarboxylates and dithiocarboxylates[11], we are concerned with the conformation of Se-alkyl seleno-carboxylates (*A* or *B*). For the dipole moment study compounds *III – VI* (Table I) were chosen; the presence of a *para*-substituent in *IV* and *VI* enabled us to apply the graphical method of evaluation[12]. Systematic comparison of similar classes of compounds[10,11,13,14] was intended to reveal factors controlling the remarkably stable and uniform conformation of carboxylic esters.

A (trans) *B (cis)*
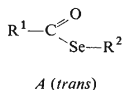
Since the conformation of diselenides is known[3–7], compounds *I* and *II* served us mainly to test both the method and the values of bond moments used.

TABLE I

Polarization and Dipole Moments of Selenium Compounds
Benzene, 25°.

No	Compound	Ref.	∞P_2 cm³	R_D cm³	μ (5%)[a] D	μ (15%)[a] D
I	$(C_6H_5Se-)_2$	15	150·9	74·8[b]	1·88[c]	1·78
II	$(4-Br-C_6H_4Se-)_2$	16	119·9	90·5[b]	1·10[c]	0·88
III	$CH_3COSeC_6H_5$	17	110·0	47·58[d]	1·72	1·65
IV	$CH_3COSeC_6H_4-Br-4$	—	176·9	55·4[b]	2·41	2·36
V	$C_6H_5COSeC_6H_5$	18	101·4	68·6[b]	1·20	1·05
VI	$4-Cl-C_6H_4COSeC_6H_5$	—	89·7	73·5[b]	0·78	0·50

[a] Correction 5% or 15%, respectively, of the R_D value was taken for the atomic polarization; [b] Calculated values, see Experimental; [c] Ref.[3] gives 1·68 D and 0·71 ± 0·3 D for I and II, respectively; [d] The experimental value at 20°; n_D^{20} 1·5964, d^{20} 1·4248.

EXPERIMENTAL AND RESULTS

Materials. Compounds *I—VI* were prepared according to literature data (Table I) or by applying standard methods. The melting points were determined on the Kofler block; samples for analysis and for measurement of dipole moments were dried at 0·2 mm Hg over P_2O_5 at room temperature.

4-Bromophenyl selenoacetate (IV). To a solution of 4-bromoselenophenol[16] (11·8 g) and dry pyridine (4 g) in benzene (25 ml), acetyl chloride (4·0 g) was added dropwise, the mixture left overnight at room temperature and washed successively with 10% HCl, 15% NaOH and water. Benzene was removed, the residue distilled *in vacuo* and the crystalline product recrystallized from light petroleum, yield 6·50 g (47%), m.p. 52—5°C. For C_8H_7BrOSe (278·0) calculated: 34·56% C, 2·54% H, 28·74% Br, 28·41% Se; found: 34·88% C, 2·51% H, 28·26% Br, 27·96% Se.

Phenyl 4-chloroselenobenzoate (VI). A solution of selenophenol (4·4 g), dry pyridine (2·25 g) and 4-chlorobenzoyl chloride (4·9 g) in benzene (10 ml) was refluxed 2 h, washed with water and benzene evaporated *in vacuo*. The residue yielded by crystallization from cyclohexane 6·25 g (75%) of product, m.p. 84—5°C. For $C_{13}H_9ClOSe$ (295·6) calculated: 52·82% C, 3·07% H, 11·99% Cl 26·71% Se; found: 53·24% C, 3·05% H, 11·77% Cl; 26·54% Se.

Measurement of dipole moments. The same method was used as previously[10–14]. Molar refractions were calculated using Vogel's atom increments[19], the increments of 10·70 and 22·32 cm³ (ref.[20]) for Se and Se_2, respectively, and estimated exaltation of 0·7 cm³ for the conjugation Se—Ph, and 1·8 cm³ for Ph—Se—Se—Ph. From the experimental refraction of compound *III* an exaltation of 0·6 cm³ for the conjugation CO—Se was then deduced (the same as for CO—S, see[11]). Finally, with compounds *V* and *VI* and additional exaltation of 1·25 cm³ was applied for the conjugation Ph—CO(Se), *i.e.* again the same as for[11] Ph—CO(S). The uncertainty in the whole procedure is large; it does, however, not markedly affect the final values of dipole moments, except for the low moment of *VI*. The experimental results are listed in Table I. The dipole moments of diselenides *I* and *II* agree reasonably with previous determinations[3]. The moments of seleno esters *III* and *IV* are close to those of corresponding oxygen[13,21] and sulfur[21] analo-

gues, while the moments of *V* and *VI* are low when compared to *III* and *IV* or to oxygen analogues[13]. The reasons for this difference are not clear.

Calculation of theoretical dipole moments. All the calculations were carried out graphically with the accuracy of ± 0.03 D. The same bond moments were used as in previous papers[10–13]: C_{al}—H 0·3 D, C_{ar}—H 0, C=O 2·5 D, C_{ar}—Cl 1·60 D, C_{ar}—Br 1·58 D, mesomeric moment for the conjugation Ph—CO 0·25 D, the moment C—Se is dealt with in the Discussion. The valence angles were $\sphericalangle$ C—C=O 116°, $\sphericalangle$ O=C—Se 124°, $\sphericalangle$ C—S₂—C 96°, $\sphericalangle$ C—Se—Se 106° (ref.[5–7,11,22]).

DISCUSSION

In order to determine the conformation of the compounds studied, the first task is estimating the appropriate moment of the C—Se bond. Since this bond is highly polarisable, its bond moment can vary from one molecule to another and has to be deduced from closely related derivatives. The two experimental values for diphenyl selenide[23] agree only fairly but a bond moment C—Se 1·15 D can be estimated at least for selenium bound to the aromatic nucleus. This value is higher than a previous estimate[3] as well as a commonly used moment of the C—S bond[10,11] although some aliphatic selenium compounds have identical moments as their sulfur analogues[24].

When the expected dipole moments for compounds *I* and *II* in various conformations are computed using this bond moment and plotted in a graph (*i.e.* μ^2 of the unsubstituted compound on the *x*-axis and μ^2 of the *para*-derivative on the *y*-axis, according to the method previously described[12]), Fig. 1 is obtained. When the two halves of the molecule rotate around the central S₂—Se bond, the corresponding
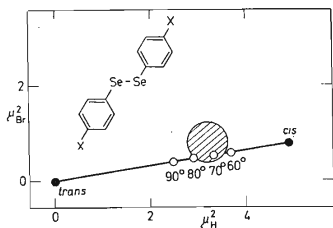

FIG. 1

Comparison of Dipole Moments of Diphenyl Diselenide *I* (*x*-Axis) and its 4,4′-Dibromo Derivative *II* (*y*-Axis)

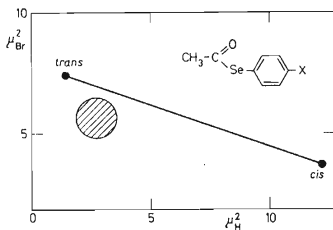Experimental point is expressed by the hatched circle, values of μ^2 are plotted on the axes[12].

FIG. 2

Comparison of Dipole Moments of Phenyl Selenoacetate *III* (*x*-Axis) and its 4-Bromo Derivative *IV* (*y*-Axis)

point in the graph moves along a straight line. By a comparison with the experimental point (assuming the same conformation of the substituted and unsubstituted compound[12]) a dihedral angle of 75° can be estimated which is in good agreement with a X-ray study[6] of I (82°), a spectral study of dimethyl diselenide[5] (82°) as well as with various previous estimates based on dipole moments[3,4].

The agreement with experiment in Fig. 1 would be still improved if we supposed that the C—Se bond is polarized under the influence of the C—Br dipole so that its bond moment is effectively lessened. The effect would be much more pronounced with the nitro group as *para*-substituent as it follows from the dipole moment of 4-nitrophenyl methyl selenide[25]. For this reason the nitro group would be not a suitable substituent in this study. Furthermore, if we attempt to determine the conformation of diphenyl disulfide on the basis of its dipole moment and those of bis-(4-bromofenyl) disulfide and diphenyl sulfide[23], exactly the same result with the same deviation is obtained as in Fig. 1. We shall not decide here to what extent this effect is due to polarization or to mesomerism; the latter possibility is preferred, of course, in the presence of the nitro group.

Based on these results, the hitherto unknown conformation of selenoesters can be determined. The expected dipole moments of selenoacetates III and IV are compared with the experimental values in Fig. 2. The agreement with experiment is only fair, particularly the experimental moment of the bromo derivative IV is less than expected. In this case neither reducing the C—Se bond moment nor introducing a mesomeric moment for the O=C—Se group[11] would help. Therefore no attempt will be made to explain this deviation. A similar picture as in Fig. 2 was obtained previously for phenyl acetate and its 4-chloro or 4-nitro derivatives[13], for which a *trans* conformation is well established. Hence an essentially *trans* conformation must be accepted for III and IV as well, even when a slight deviation from planarity, say up to the dihedral angle of 30°, cannot be excluded. The somewhat less reliable result is confirmed by a much more convincing one in the case of selenobenzoates V and VI (Fig. 3). Here the substituent is not directly conjugated with the functional group and the agreement of experimental

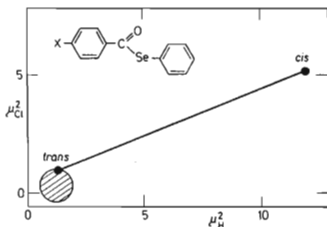FIG. 3

Comparison of Dipole Moments of Phenyl Selenobenzoate V (x-Axis) and Phenyl 4-Chloro-selenobenzoate VI (y-Axis)

values with those calculated for the *trans* conformation is excellent. Likewise when determining the conformation of carboxylic esters[13] and thioesters[11], substitution in the acid part of the molecule proved to be most suitable.

We conclude that our results do not reveal any difference in the conformation of selenoesters when compared to thioesters and oxygen esters. The factors controlling this remarkably stable conformation were previously discussed in some detail[11]. The mesomerism within the functional group was considered to be the decisive factor responsible for the planarity of the molecule, while the repulsion of lone electron pairs favours the *trans* over the *cis* conformation. If it is true, the mesomerism in the —CO.Se— group is of similar importance as in the —CO.S— and —CO.O— groups and, in addition, the electrostatic repulsion is not significantly reduced by the size of the selenium atom.

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