DIPOLE MOMENTS OF CYCLIC ESTERS OF SELENOUS ACID

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The structure of cyclic esters of selenous acid has been very little studied; there are data only on the structure of ethyleneselenite [1] and trimethyleneselenite [2].

Continuing investigations of the conformation of cyclic compounds, we measured the dipole moments (DM) of certain five and six-membered cyclic esters of selenous acid. Table 1 presents the values of the DM (μ in debyes) of five-membered selenites and the corresponding sulfites. A comparison of these values shows that five-membered cyclic selenites and the corresponding sulfites should have similar structures; the small constant difference in the DM (~0.3-0.4 D) of the sulfur and selenium analogs can be explained by a difference in the DM of the bonds of sulfur and selenium. As can be seen from Table 1, in the series of sulfites and selenites the change in the DM due to the introduction of methyl groups occurs analogously, which can be explained, in all probability, by the positive inductive effect of these groups.

As is well known, for a long time there was no single opinion concerning the conformations of cyclic six-membered sulfites. Recently it was shown in [4-6] that the chair conformation with axial arrangement of the S = O bond is preferential for six-membered sulfites. A consideration of the DM of the unshared pair of electrons of the sulfur atom proved extremely important in the calculation of the DM [7]. In connection with this, it proved to be of interest to study the conformation of six-membered cyclic esters of selenous acid. We synthesized 2,2-dimethyl-, 2-chloro-, 2-nitro-, as well 1,1,3,3-tetramethylpropanediolselenites and measured their DM (Table 2). However, a conformational analysis of these compounds by the DM method proved difficult in view of the following factors. The DM of a central Se = O bond and the moment of the unshared pair of electrons of the selenium atom are unknown. The dipole moment of the Se = O bond was calculated from the moment of selenium oxychloride, using a number of assumptions [8] and in the absence of consideration of the DM of the unshared pair of selenium, which unquestionably introduces an inaccuracy into the moment of this bond.

It is interesting to compare the experimental DM of six-membered cyclic sulfites and selenites (see Table 2). For the latter the DM also are approximately 0.9 D lower. This difference in the experimental

TABLE 1	l
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	Δμ, D		Δμ, D	$\Delta \mu$ in series, D		
Compound	X=Se	X=S	of ana- logs	X=Se	X=S	
$\begin{array}{c} CH_2 \rightarrow 0 \\ \downarrow \\ CH_2 \rightarrow 0 \end{array} X = 0 \end{array}$	3,31*	3,65 [3]	0,34	0.23	0.19	
$CH_{a}-CH=0$ I $CH_{a}=0$	3,54	3,84	0,30	0.91	0.30	
$CH_3-CH=0$ $CH_3-CH=0$ X=0	3,75	4,14	0,39	0,21	0,50	
(CH ₃) ₂ C-0 (CH ₃) ₂ C-0 X=0	4,11	4,54	0,43	0,36	0,40	
The values 3.35 and 3.87 D were cited in [1].						

DM is considerably higher than the difference in the DM for five-membered cyclic sulfites and selenites and cannot be explained solely by a difference in the DM of the bonds of sulfur and selenium.

EXPERIMENTAL

Cyclic selenites were synthesized by the interaction of the corresponding glycols with selenous acid in a suitable solvent or without it.

Ethyleneselenite was produced according to the well-known procedure [9]; bp $70-72^{\circ}$ (0.16-0.17 mm); mp 65-66°. According to the data of [1]: bp 115° (3 mm); mp 64-65°; [10]: mp 66°.

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TABLE 2

	μ, D			
Compound	X=S	X=Se	Δμ, D	
$CH_2 < CH_2 - 0 CH_2 - 0 CH_2 - 0 X = 0$	3,60 [3]	2,50*	0,90	
$CH_{s} CH_{2} C CH_{2} O X=0$	3,44	2,52	0,92	
$Cl-CH \begin{pmatrix} CH_2-O \\ CH_2-O \end{pmatrix} X = O$	2,84	1,96	0,88	
$NO_2-CH \left\langle \begin{array}{c} CH_2-O\\ CH_2-O \end{array} \right\rangle X = 0$	3,12	2,37	0,75	

* We measured the DM; in [1] two values are cited: 2.50 and 3.02 D.

Propyleneselenite was produced using the method of [9]: bp 34.8-35.4° (0.05 mm); d_4^{25} 1.8699; n_D^{25} 1.5242; MR found 27.66, MR calculated 27.55. According to the data of [10]: bp 104° (3 mm); d_4^{20} 1.9086; n_D^{20} 1.5308.

2,3-Butanediolselenite was synthesized according to [9]; bp 90-91.5° (5.5 mm); d_4^{25} 1.7023; n_D^{25} 1.5108; MR found 32.30, MR calculated 31.96. Found: Se 43.64%. C₄H₈SeO₃. Calculated: Se 43.13%.

<u>Tetramethylethyleneselenite</u>. Produced by heating equimolar amounts of dehydrated pinacol and selenous acid on an oil bath (180°) for 40 min. Repeated recrystallization from CCl_4 gave a selenite with mp 114.5-115.5°. Found: Se 37.27%. $C_6H_{12}SeO_3$. Calculated: Se 37.42%. Yield of the crude product 84%.

<u>Trimethyleneselenite</u>. Produced according to the method of [9]; bp 80-81° (4 mm); mp 88-89°. Found: Se 46.33%. $C_3H_6SeO_3$. Calculated: Se 46.71%. Yield of the pure product 39%.

2,2-Dimethylpropanediolselenite. Produced from 2,2-dimethylpropanediol and selenous acid according to the method of [9]; bp 63° (6 mm); mp 84-85.3°. Found: Se 40.31%. $C_5H_{10}SeO_3$. Calculated: Se 40.06%. Yield of the purified product 15%.

<u>2-Chloropropanediolselenite</u>. A mixture of the α - and β -chlorohydrins of glycerine, produced according to the method of [11], was redistilled on a fractional distillation column with an efficiency of 17 theoretical plates after distillation under vacuum. The fraction with bp 99-101° (6.5 mm) and nD²⁵ 1.4820 was collected. A mixture of 7 g of the β -chlorohydrin of glycerine, 8.97 g selenous acid, and 200 ml of benzene was heated in a flask equipped with a Dean – Stark trap at a bath temperature no higher than 140°. After 1 h had elapsed, the benzene was distilled off under vacuum. The dense oil remaining crystallized upon cooling. The crystals, preliminarily pressed out on a filter, were sublimed twice under vacuum (5 mm) at a temperature no higher than 112°. After recrystallization from abs. benzene, mp 157-159°. Found: C 17.65; 17.75; H 2.39; 2.51%. C₃H₅SeO₃Cl. Calculated: C 17.71; H 2.47%. Yield of the purified product 15.5%.

<u>2-Nitropropanediolselenite</u>. For the synthesis of 2-nitropropanediol-1,3, its sodium derivative, produced according to [12], was treated with salicylic acid [13]. A mixture of 6 g of the diol, 7.03 g selenous acid, and 700 ml of benzene was boiled in a flask equipped with a Dean – Stark trap under a slight vacuum (200 mm). The bath temperature was maintained no higher than 74°, temperature of the mixture 60°. After 3.5 h the reaction mixture was cooled to 35° and the benzene solution filtered. The crystals that precipitated when the solution was cooled were purified by repeated washing with abs. ether, then by sublimation under high vacuum at a bath temperature no higher than 80°; mp 107-108° (with dec.). Found: C 16.85; 17.11; H 2.58; 2.40; Se 36.99%. C₃H₅NO₅Se. Calculated: C 16.84; H 2.35; Se 36.89%. Yield of the purified product 18.3%.

The compound is very hygroscopic and decomposes rapidly in air, liberating red selenium; therefore the preparation of the solutions for measurement of the DM, weighing of samples for analysis, and filling of the capillary to determine the melting points were performed in a dry box with nitrogen, dried with P_2O_5 .

<u>1,1,3,3</u>-Tetramethylpropanediolselenite. For the synthesis of this compound we produced 1,1,3,3tetramethylpropanediol-1,3 according to the method of [13] by reducing diacetone alcohol with Grignard reagent. A mixture of 5 g of the diol and 5,36% selenous acid (10% excess) in 650 ml abs. benzene was boiled in a flask equipped with a Dean – Stark trap under slight vacuum (200 mm) for ~3 h. The crude benzene solution was decanted from the unreacted precipitate, and the benzene evaporated under vacuum under nitrogen. The residue was redistilled under high vacuum; bp 44.5-45° (0.01 mm). The colorless liquid in the receiver crystallized when the latter was lowered into a cool mixture of ice and salt. Four grams of a white crystalline substance was obtained, which immediately deliquesced in air, probably as a result of its strongly hygroscopic properties. Found: C 36.59; 36.64; H 5.77; 5.61; Se 35.62%. C₇H₁₄SeO₃. Calculated: C 37.34; H 6.28; Se 35.07%.

TABLE 3

Compound	81	d,	α	β	₽2 _∞	Pc	μ, D
2 ,2- Dimethylpropanediolselenite	2,27555	0,87456	8,70313	0,94211	165,069	130,289	2,52
2-Chloropropanediolselenite	2,22419	1,02681	5,75083	1,14320	112,709	78,794	1,96
2-Nitropropanediolselenite	2,22740	1,02630	8,67175	1,52134	148,577	115,147	2,37
1,1,3,3-Tetramethylpropanediol- selenite	2,20713	1,02945	20,47138	0,57232	362,531	316,171	3,93
Propyleneselenite 1,2-Dimethylethyleneselenite	2,273 45 2,27873	0,87279 0,87313	17,39211 19,78440	1,09133 1,07490	284,311 319,787	256,643 287,579	3,54 3,75
Tetramethylethyleneselenite	2,28122	0,87335	23,57988	0,98585	386,950	345,870	4,11
Tetramethylethylenesulfite	2,27336	0,87325	28,32474	0,43917	457,731	421,471	4,54

<u>Tetramethylethylenesulfite</u>. Produced by drop-wise addition of 0.12 mole of freshly redistilled thionyl chloride to a mixture of equimolar amounts of dehydrated pinacol and triethylamine in ether solution over a period of 2.5 h. The product was extracted with ether. The precipitate of triethylaminehydrochloride was filtered, and after the ether was distilled off, the crystalline product was redistilled under vacuum. The fraction with bp 81-87.5° (15 mm) was redistilled again. A white crystalline substance with bp 88.5-89° (16 mm) and mp 44-45° was obtained. Found: S 19.46%. $C_6H_{12}SO_3$. Calculated: S 19.52%.

The DM were measured at $25 \pm 0.1^{\circ}$. For most of the compounds benzene was used as the solvent. As a result of low solubility in benzene, the DM of 2-chloro-, 2-nitro-, and 1,1,3,3-tetramethylpropanediolselenite were measured in dioxane. The total polarization of the dissolved substance at infinite dilution was found according to the Gedestrand equation. The atomic polarization was not taken into consideration. The error in the measurement of the DM was ± 0.02 D. Table 3 presents the dielectric permeability ε_1 and d_1 of the solvent, the coefficients in the Gedestrand equation α and β , the values of the total polarization of the substances at infinite dilution $P_{2\infty}$ and the orientational polarization P_0 , as well as the experimentally found values of DM in debyes.

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CONCLUSIONS

1. Previously undescribed 1,2-dimethyl- and tetramethylethyleneselenites, tetramethylethylenesulfite, 2,2-dimethyl-, 2-chloro-, 2-nitro-, and 1,1,3,3-tetramethylpropanediolselenites were produced.

2. The dipole moments of propylene selenite and the compounds enumerated above were determined.

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