

tions were applied. The absorption corrections were carried out according to a procedure by Coppens, Leiserowitz and Rabinovich.⁷ The dimensions of the intensity crystal were $0.39 \times 0.04 \times 0.04$ mm in the three axial directions. A grid of $32 \times 4 \times 4$ points was used.

The atomic parameters were refined by a full-matrix least squares procedure, and the final *R* factor is 0.12. Anisotropic temperature factors were applied to selenium, sulphur, and carbon, and isotropic to hydrogen. The hydrogen positions were not refined.

Final atomic coordinates from the least squares refinement are listed in Table 1.

Table 1. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.05316(28)	0.25000	0.2248(3)
S	0.06777(72)	0.09766(32)	0.1904(12)
C(1)	0.1850(23)	0.0993(12)	-0.0622(42)
C(2)	0.2364(26)	0.1715(12)	-0.1661(32)
C(3)	0.1956(26)	0.2500	-0.0661(39)
H(1)	0.2096	0.0499	-0.1267
H(2)	0.2920	0.1746	-0.2996

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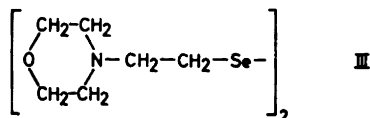
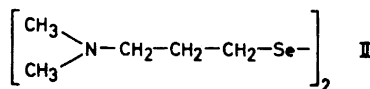
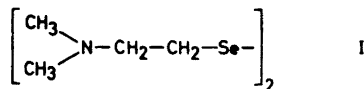
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Diseleno Derivatives of Some Amines

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The diselenides I–III and some related compounds have been prepared in order to test their activity in preventing dietary liver necrosis in rats (factor-3-effect).¹ This effect is found in various organoselenium compounds and many diselenides show good potency.^{2,3} Compounds with tertiary amino groups like those in I–III are often



pharmacologically active and it was therefore of interest to study the influence of such amino groups upon the factor-3-activity of diselenides. It turned out, however, that the potency of the compounds was remarkably low, even compared to that of inorganic selenites.

Synthesis in the ordinary way from chlorosubstituted amines and alkali diselenide solutions gave rather impure products, obviously contaminated with mono- and/or triselenides. Such complications have been observed in other cases. In addition, decomposition during the purification is not uncommon and even rearrangements have been reported.⁴ It seems that the amino group makes the diselenide less stable. Attempts to oxidise the amines to aminoseleninic acids led to cleavage of the C–Se bond, yielding selenous acid.

Table 1.

	Formula	Se calc.	Se found
Di(2-dimethylaminoethyl)-diselenide dipicrate	$C_{20}H_{26}N_8O_{14}Se_2$	20.77	20.58, 20.55
Di(2-dimethylaminoethyl)-diselenide dihydrobromide	$C_8H_{22}Br_2N_2Se_2$	34.03	34.11, 34.12
Di(3-dimethylaminopropyl)-diselenide dipicrate	$C_{22}H_{30}N_8O_{14}Se_2$	20.03	20.18, 20.07
Di(3-dimethylaminopropyl)-diselenide dihydrobromide	$C_{10}H_{26}Br_2N_2Se_2$	32.09	32.02, 32.08
Di(2-N-morpholinylethyl)-diselenide	$C_{12}H_{24}N_2O_2Se_2$	40.88	40.74, 40.75

The following amines were isolated as dipicrates but the purity was not satisfactory:

Di(2-diethylaminoethyl)-diselenide	Di(2-N-piperidylethyl)-diselenide
Di(3-N-morpholinylpropyl)-diselenide	Di(3-N-piperidylpropyl)-diselenide

Compounds I–II could be obtained in a pure state as salts and compound III as the free base. Four other compounds (specified in connection with Table 1) were isolated as dipicrates but the content of selenium was either too high or too low; the deviations amounted to 5–10% of the calculated values. Since preliminary experiments showed that the potency of these compounds was low and rather close to that of compounds I–III no further attempts to purify them were made.

Preliminary experiments indicated that the salts of hydrochloric, sulphuric, and acetic acid were easily soluble and difficult to handle.

The work on the factor-3-effect is carried out in collaboration with Professor Klaus Schwarz* and will be published and discussed elsewhere.

Experimental. General procedure. An aqueous solution of sodium diselenide was prepared in the usual way from selenium, sodium hydroxide, and Rongalite. The chlorosubstituted amine (commercial product) was added and the solution refluxed under nitrogen until the dark reddish brown colour has changed to pure yellow. Sodium carbonate in excess was

added and the solution extracted 4 times with ether. Only the morpholinyl derivative III was crystalline at room temperature; after recrystallisations from petroleum ether it was obtained as yellow rod-shaped crystals. The other amines were isolated as picrates or hydrobromides forming yellow rods or needles.

The dipicrates were obtained by mixing dilute solutions of amine and excess picric acid in dry ether. The dihydrobromides were prepared from amine and aqueous hydrobromic acid. After evaporation of the solvent, the salt was dried and recrystallised several times from butanol. If elemental selenium separated, it was removed by filtration. The analytical data are given in Table 1.

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