

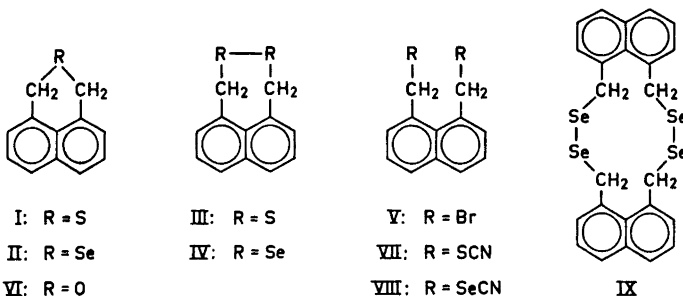
Some Sulphur and Selenium Compounds Derived from 1,8-Dimethylnaphthalene

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The compounds I and II have been synthesised and their NMR-spectra studied. Attempts to prepare compound III gave amorphous products, probably high polymers. The corresponding selenium compound (IV) seems to exist for a short time in solution, but is rapidly transformed to the well-characterised dimer IX, which has a 14-membered heterocyclic ring.

In connection with previous work on simple ring systems containing sulphur and/or selenium¹⁻⁴ it was desirable to study the compounds I-IV. In both types, the methylene carbons should be situated approximately in the plane of the aromatic ring system. In I and II, the hetero atoms are probably located out of this plane (Fig. 1). The same must be true for the hetero atoms in III and IV, but, considering the rigid carbon system and the dihedral angles of the disulphide and diselenide groups, these rings should be rather strained. A strong tendency to polymerisation, giving larger rings or chain polymers, could therefore be expected.



Attempts to prepare the naphthothiopyrane I in the conventional way from 1,8-bisbromomethyl-naphthalene (V) and sodium sulphide in ethanolic solution gave apparently homogeneous, crystalline products with rather

sharp melting-points. However, both the melting-points and the sulphur contents (which were always too low) varied from one experiment to another. NMR showed (besides the signals from the aromatic protons) two sharp frequencies at 4.78 and 3.73 ppm. The former was due to contamination with the oxygen compound VI (comparison with an authentic specimen prepared according to Weinheimer *et al.*⁵). Synthesis in super-dry ethanol under strictly anhydrous conditions gave the pure sulphur compound (I) with m.p. 96–97° and a singlet at 3.73 ppm. It is obvious that more or less of the oxygen compound is formed if hydroxyl ions are present. With the sulphur compound it gives solid solutions with rather sharp melting points, and it cannot be removed by recrystallisation.

Experiments with sodium selenide gave quite analogous results: only synthesis under strictly anhydrous conditions yielded the pure naphthoselenopyrane (II) with m.p. 83.5–84.5° and a singlet at 3.76 ppm.

If the hetero atom in I or II is situated out of the plane of the carbon system (Fig. 1), the methylene protons are not equivalent, and in NMR an AB quartet

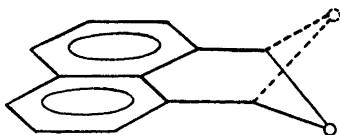


Fig. 1.

may be expected. Since only one signal was observed, there must be a rapid oscillation between the two possible positions of the hetero atom. The selenium compound, having the heaviest hetero atom, was therefore examined at lower temperatures. From –80° an obvious broadening of the signal was observed, but measurements below –100° were not possible owing to insufficient solubility at these temperatures.

Attempts to prepare the disulphide III from the bromo compound V and sodium disulphide or polysulphides gave only mixtures of the monosulphide I, the oxygen compound VI and amorphous, smeary products. Reaction with potassium xanthate gave no well-defined compounds, but with sodium thiocyanate the compound VII was obtained as large crystals with m.p. 130–131°. However, all attempts to convert it to a disulphide gave only amorphous, probably high polymeric products. On the other hand, the existence of the monomeric disulphide in solution as a short-lived intermediate cannot be excluded.

The biselenocyanato compound (VIII) was easily obtained as large crystals with m.p. 117–119°. Treatment with potassium hydroxide in methanol, which should give the diselenide, gave first a dark red solution. The colour faded rapidly, and a pale yellow crystalline powder separated. It had the expected composition, but owing to its very low solubility the molecular weight could not be determined by current methods. Even the Rast method, using camphor, anthracene or phenanthrene as solvents, gave no results. The mass spectrum showed no distinct molecular peak.

The low solubility indicated a polymer. The rather well-developed crystals excluded a high polymer, and in such case the dimer IX was nearest at hand.

An X-ray study of the crystal structure, performed by Dr. S. Aleby, has fully confirmed this anticipation.⁶ This work will be published elsewhere.

Acylic diselenides with normal dihedral angle are yellow, having an absorption band with λ_{\max} around 300 nm.⁷ In diselenide rings, where the dihedral angle may deviate from its normal value, the absorption is shifted to higher wave-lengths and the colour is more or less red. The 6-membered 1,2-diselenane rings have λ_{\max} at 340–365 nm,⁷ and the 5-membered 1,2-diselenolane rings at 440–450 nm.^{1,3,7} The red solution mentioned above showed λ_{\max} at 415 nm, while the compound IX was too insoluble to permit any spectral studies.

The observations indicate that the primary product, giving the deep red solution, is the monomer IV with a strained 7-membered ring. It very rapidly dimerises to the pale yellow compound IX, where the 14-membered ring will permit a normal dihedral angle.

Very few measurements of dihedral angles in diselenides could be found in the literature. The data suggest that the angle is not far from 90°, but can lie on either side of this value. For the compound IX, Aleby⁶ reports the preliminary value $92 \pm 2^\circ$. The naphthalene rings are planar, and the angle between the two planes is near 90°.

EXPERIMENTAL

The NMR spectra were studied on a Varian A 60 instrument and the UV-spectra on a Hitachi Perkin-Elmer 139 spectrophotometer. Analyses for carbon, hydrogen, and sulphur were carried out by the Analytical Department of the Institute.

1,8-Bisbromomethyl-naphthalene (V). This compound was prepared from naphthalic acid anhydride over the dihydroxy compound, following known procedures.^{8,9}

1H,3H-Naphtho-[1,8]-thiapyrane (I). Sodium ethanolate was prepared from sodium (2.3 g, 0.1 mol) in super-dry ethanol under dry, oxygen-free nitrogen. One half of the ethanolate was transferred to a dropping funnel, and hydrogen sulphide was bubbled through the residual solution for 1 h. Then the ethanolate was added from the dropping funnel. 1,8-Bisbromomethyl-naphthalene (12.5 g, 0.04 mol) was dissolved in super-dry ethanol (400 ml), and the sodium sulphide solution was added dropwise over 15 min. The reaction mixture was refluxed for 15 min and left at room temperature over-night under dry, oxygen-free nitrogen. The solvent was evaporated and the residue was extracted several times with boiling petroleum ether (b.p. 70°). The solvent was evaporated to leave 6.5 g of a colourless, partly oily solid. Recrystallisation from petroleum ether (b.p. 70°) yielded 4.5 g (0.024 mol, 60 %) of the pure product as colourless crystals with m.p. 96–97°. (Found: C 77.34; H 5.42; S 17.11. Calc. for C₁₂H₁₀S: C 77.37; H 5.41; S 17.22.)

1H,3H-Naphtho-[1,8]-selenin (II). Sodium ethanolate was prepared from sodium (2.3 g, 0.1 mol) in super-dry ethanol under dry and oxygen-free nitrogen. Hydrogen selenide, prepared from aluminum selenide and dried over Siccapent, was bubbled through the solution for 1.5 h. The increase of weight was 4 g. The sodium selenide solution was transferred to a dropping funnel. 1,8-Bisbromomethyl-naphthalene (15.5 g, 0.05 mol) was dissolved in super-dry ethanol (400 ml), and the sodium selenide solution added dropwise over 15 min. The reaction mixture was kept dark and allowed to stand at room temperature for 48 h under a dry and oxygen-free atmosphere. The solvent was evaporated and the residue extracted several times with boiling petroleum ether (b.p. 70°). Evaporation of the solvent yielded 8 g of a partly oily solid. Three recrystallisations from petroleum ether (b.p. 70°) yielded the pure product, 4 g (0.017 mol, 34 %) with m.p. 83.5–84.5°. (Found: C 61.84; H 4.31; Se 33.8. Calc. for C₁₂H₁₀Se: C 61.81; H 4.32; Se 33.87.)

1,8-Bis-thiocyanatomethyl-naphthalene (VII). 1,8-Bisbromomethyl-naphthalene (9.5 g, 0.03 mol) was dissolved in acetone (200 ml), and potassium thiocyanate (7.5 g, 0.07 mol) dissolved in acetone (100 ml) was added. The mixture became hot, and was refluxed for

10 min. The potassium bromide was filtered off and the solvent was evaporated. The residue was recrystallised twice from benzene-ligroin (1:3) to yield 7 g (0.027 mol, 90 %) of the pure product with m.p. 130–131°. (Found: C 64.33; H 3.81; S 24.59. Calc. for $C_{14}H_{10}N_2S_2$: C 64.57; H 3.87; S 24.64.)

1,8-Bisselenocyanatomethyl-naphthalene (VIII). 1,8-Bisbromomethyl-naphthalene (18.8 g, 0.06 mol) was dissolved in acetone (300 ml), and potassium selenocyanate (20.2 g, 0.014 mol) dissolved in acetone (200 ml) was added. The mixture became hot and was refluxed for 10 min. The potassium bromide was filtered off, and the solvent was evaporated. Two recrystallisations from benzene-ligroin (1:2) yielded 19 g (0.052 mol, 87 %) of the pure product with m.p. 117–119°. (Found: C 46.22; H 2.79; Se 43.4. Calc. for $C_{14}H_{10}N_2Se_2$: C 46.18; H 2.77; Se 43.37.)

Dimer of 1H,4H-naphtho-[1,8]-diselenepin (IX). 1,8-Bisselenocyanatomethyl-naphthalene (1.2 g, 0.003 mol) was dissolved in methanol (50 ml), and potassium hydroxide (0.1 g) dissolved in methanol (10 ml) was added. The solution instantly became deep red but decolourised within a few minutes, while pale yellow needle-shaped crystals separated. 0.9 g (0.0014 mol, 93 %) was obtained. Recrystallisation of 0.3 g required 800 ml xylene. M.p. 220°. (Found: C 46.22; H 3.21; Se 50.6. Calc. for $(C_{12}H_{10}Se_2)_2$: C 46.18; H 3.23; Se 50.59.)

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