distortion of the diselenane molecule is observed, but a minor deformation is indicated in the case of particularly strong Se⋯I bonds (in the iodine compound) and when each sulphur atom forms two bonds to iodine, from a shortening of the intramolecular Se⋯Se distance by a few hundredths of an Å. The four iodine atoms form a nearly rectangular, with sides 3.33 and 3.68 Å long. The carbon coordinates are of course not so accurately determined, but it appears that the C–C bond direction runs approximately parallel to the longer side of the iodine rectangle and the C–I distance and the angle ICI are not sensitive to a deviation from strict parallelism. Assuming the C–C distance to be 1.34 Å the figures obtained are C–I = 2.12 Å, the angle ICI = 113°.

The crystals belong to the space group P2₁/c and the lattice parameters are: a = 6.50, b = 12.80, c = 9.21, β = 99.6°. The number of formula units in the unit cell is 2. The intensity data for the 0kl zone were collected from integrated Weissenberg diagrams and measured photometrically. For the h0l zone a diffractometer with counter was employed. Absorption corrections were applied in both cases, although MoKα-radiation was used. The final R factors were 5.5% (0kl) and 7.7% (h0l).

In Fig. 1 the Fourier map for the a-axis projection is reproduced and visualizes the chains of alternating donor and acceptor molecules running along the [101] direction.

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Preparation of [¹⁵N]- and [⁴¹⁸C]-Pyridine

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As a pre-requisite for the determination of the r₁-structure of pyridine by microwave technique, milligram quantities of [¹⁵N]- and [⁴¹⁸C]-pyridine were prepared.

[¹⁵N]-Pyridine. Anhydrous sodium glutaconialdehyde (1) was prepared. A 32% yield has been claimed. The yields obtained by us varied between 10 and 25%. 640 mg 33% enriched ¹⁵NH₄NO₃ (8 mmole) was dissolved in 240 ml dry methanol to which 8 g anhydrous MgSO₄ was added for immediate removal of water under the subsequent reaction. After 15 min of stirring, 9.5 g (80 mmole) (1) was added. The flask was closed and left to itself at room temperature for 2 weeks under continued stirring. MgSO₄ was separated by filtering and washed by methanol. 10 ml 12 N aqueous HCl was added to the combined methanolic solutions, from which methanol was removed in vacuo. The almost dry residue was again dissolved in 14 ml 4 N HCl and the water and the remaining methanol removed in vacuo. For separation from polymerized glutaconialdehyde the residue was dissolved in 7 ml 4 N HCl and transferred to a Claysen flask together with 2 g NaOH. At 1 atm, 50 ml water-pyridine-ammonia mixture was distilled off into 14 ml 4 N HCl. The water was removed in vacuo at a final temperature of 40°C and the residue transferred with 250 ml water to an Erlenmeyer flask. 1 g KBr and 0.5 g NaHCO₃ was added and dissolved. A small quantity of ammonia was oxidized to nitrogen by addition of 2 ml of a solution containing 0.4 mmole OCl⁻ per ml. Hereafter, water and bromine was removed in vacuo. A solution of 3 g NaOH in 70 ml water was added, and 50 ml water-pyridine mixture was distilled off at 1 atm into 14 ml 4 N HCl. After renewed evaporation to dryness, the residue was dissolved in 0.7 ml water. A warm solution of 1.1 g HgCl₂ in 7 ml water was added. The crystalline precipitate, C₃H₅N, HCl,
2 HgCl₄, formed during 2 hours' cooling at 0°C was filtered off and air-dried on a sintered glass-filter plate. For liberation of pyridine, the crystals were mixed with 0.7 ml saturated NaOH solution in a tube connected to a vacuum line. In the closed tube the mixture was stirred mechanically for 1 h at room temperature. Then, water and pyridine was distilled off in vacuo into a trap, cooled in liquid nitrogen by gradually raising the outside temperature of the test tube to 150°C. In the trap, the water-pyridine mixture was brought into contact with 5 g CaO at room temperature for 12 h. Two subsequent distillations over 1 g portions of CaO after contact for 1 h sufficed to produce 30 mg of a dry mixture of 33 % [¹⁴N]-pyridine and 67 % ordinary pyridine as evidenced by the vapor-pressure of the sample, a gaschromatographic analysis, and by the microwave spectrum recorded afterwards. The yield, 30 mg (0.38 mmole), is only 5% with respect to the NH₄NO₃ applied. This is due to a mishap during the drying with CaO. We know from several test experiments carried out by us on non-enriched ammonium salt, that a reproducible yield of 10 - 13 % can be obtained by the method indicated above.

[¹⁴C]-Pyridine. Following Weygand and Linden, we reduced ¹³C-enriched CO₂ from 53 % enriched BaCO₃ (2.35 g or 12 mmole) to enriched CH₄O (5.4 mmole). The resulting tetrahydrofuran solution of CH₄O was reacted with CH₂COCH₂COOCH₃ and NH₃ to yield 985 g (3.8 mmole) 3,5-dicarbethoxy-2,6-dimethyl-1,4-dihydropyridine, "marked" at 4°C. By means of Br₂CCl₃, the whole quantity was oxidized to 3,5-dicarbethoxy-2,6-dimethylpyridine also marked at 4°C. Yield 835 mg (3.2 mmole). Saponification of this quantity, neutralization by dilute HNO₃ and subsequent oxidation by 2.2 g KMnO₄ in 100 ml water at 100°C produced [¹⁴C]-pyridine-2,3,5,6-tetrahydroxy acid (II), the silver salt of which was precipitated. Yield 1.7 g (2.3 mmole). Boiling of this quantity at 100°C for 20 min with 10 ml 1 N HCl produced an aqueous solution of (II), from which water was removed completely in vacuo by gradually raising the exterior temperature to 80°C. Yield 500 mg of (II) or 2 mmole. Since the following procedure for the total decarboxylation of (II) to pyridine may not be as reproducible as desired, we shall report only the result of a single successful experiment: 184 mg (II) (0.7 mmole) dissolved in 6.5 ml quinoline with 70 mg CuO added as a catalyst was decarboxylated at atmospheric pressure and 250°C. The evolution of CO₂ stopped after 2 h. The reaction vessel was connected to a vacuum line, cooled, evacuated, and again heated to room temperature. Under internal magnetic stirring the vapors in equilibrium with the reaction mixture were distilled off over a period of 6 h into a trap, cooled in liquid nitrogen. The distillate is a mixture of quinoline, water, and pyridine. After three further distillations in vacuo over 1 g portions of CaO and one final single-plate distillation, an almost pure sample of 53 % [¹⁴C]-pyridine and 47 % ordinary pyridine was obtained, contaminated by 2 – 3 % quinoline and 4 – 5 % water as evidenced by its vapor-pressure, the infrared spectrum of the liquid, a gas-chromatographic analysis, and a subsequent microwave investigation. The yield was 44 mg (0.55 mmole).


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