

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 lengthening of the intramolecular Se...Se distance by a few hundredths of an Å U.<sup>3-5</sup> The four iodine atoms form a planar rectangle with sides 3.53 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 parallelity. 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  $P2_1c$  and the lattice parameters are:  $a = 6.50$ ,  $b = 12.80$ ,  $c = 9.21$ ,  $\beta = 99.6^\circ$ . 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 photo-metrically. For the  $h0l$ -zone a diffractometer with counter was employed. Absorption corrections were applied in both cases, although MoK-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  $[10\bar{1}]$  direction.

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## Preparation of [<sup>15</sup>N]- and [4-<sup>13</sup>C]-Pyridine

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As a pre-requisite for the determination of the  $r_s$ -structure of pyridine by microwave technique, milligram quantities of [<sup>15</sup>N]- and [4-<sup>13</sup>C]-pyridine were prepared.

[<sup>15</sup>N]-Pyridine. Anhydrous sodium glutacondialdehyde (I) was prepared.<sup>1,2</sup> A 32 % yield has been claimed. The yields obtained by us varied between 10 and 25 %. 640 mg 33 % enriched <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> (8 mmole) was dissolved in 240 ml dry methanol to which 8 g anhydrous MgSO<sub>4</sub> was added for immediate removal of water under the subsequent reaction. After 15 min of stirring, 9.5 g (80 mmole) (I) was added. The flask was closed and left to itself at room temperature for 2 weeks under continued stirring. MgSO<sub>4</sub> 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 glutacondialdehyde 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 NaHCO<sub>3</sub> 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<sup>-</sup> 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 HgCl<sub>2</sub> in 7 ml water was added. The crystalline precipitate, C<sub>5</sub>H<sub>5</sub>N, HCl,

2 HgCl<sub>2</sub>, 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 % [<sup>15</sup>N]-pyridine and 67 % ordinary pyridine as evidenced by the vapor-pressure of the sample, a gas-chromatographic analysis, and by the microwave spectrum recorded afterwards. The yield, 30 mg (0.38 mmole), is only 5 % with respect to the NH<sub>4</sub>NO<sub>3</sub> 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.

[4-<sup>13</sup>C]-Pyridine. Following Weygand and Linden<sup>3,4</sup> we reduced <sup>13</sup>C-enriched CO<sub>2</sub> from 53 % enriched BaCO<sub>3</sub> (2.35 g or 12 mmole) to enriched CH<sub>2</sub>O (5.4 mmole). The resulting tetrahydrofuran solution of CH<sub>2</sub>O was reacted<sup>5,6</sup> with CH<sub>3</sub>COCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub> and NH<sub>3</sub> to yield 0.95 g (3.8 mmole) 3,5-dicarbethoxy-2,6-dimethyl-1,4-dihydropyridine, "marked" at 4-C. By means of BrCCl<sub>3</sub>, the whole quantity was oxidized<sup>7</sup> to 3,5-dicarbethoxy-2,6-dimethylpyridine also marked at 4-C. Yield 835 mg (3.2 mmole). Saponification<sup>8</sup> of this quantity, neutralization by dilute HNO<sub>3</sub> and subsequent oxidation by 2.2 g KMnO<sub>4</sub> in 100 ml water at 100°C produced [4-<sup>13</sup>C]-pyridine-2,3,5,6-tetracarboxylic acid (II), the silver salt of which was precipitated. Yield 1.7 g (2.3 mmole). Boiling of this quantity at 100° 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 235°C. The evolution of CO<sub>2</sub> 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 % [4-<sup>13</sup>C]-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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