

6,6'-Bis-(2-pyridyl)-3,3'-thiodipyridine

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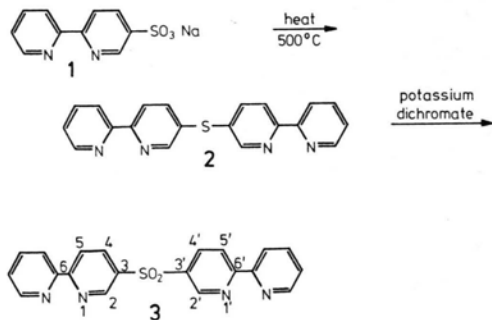
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3,3'-Thiodipyridine, 2,2'-Bipyridyl Derivative

6,6'-Bis-(2-pyridyl)-3,3'-thiodipyridine, the first example of a 3,3'-thiodipyridine, has been prepared by heating the sodium salt of 2,2'-bipyridyl-5-sulphonic acid at 500–600 °C.

2,2'- and 4,4'-Thiodipyridines¹ have been prepared many times. There appears to be no report, however, of the synthesis of a 3,3'-thiodipyridine although 5,5'-thiodi-2-pyridone² and the N,N'-dioxide of a nitro-substituted 3,3'-thiodipyridine have been described³. We now report the preparation of 6,6'-bis-(2-pyridyl)-3,3'-thiodipyridine (2).

On heating the sodium salt of 2,2'-bipyridyl-5-sulphonic acid (1)⁴ at 500–600 °C in a stream of nitrogen a brown oil was carried over along with the nitrogen. It solidified on cooling. This product was assigned structure 2, 6,6'-bis-(2-pyridyl)-3,3'-thiodipyridine, on the following evidence. Structure 2 is in accord with the elemental analyses and with the mass of the molecular ion in the mass spectrum. The NMR spectrum consisted of a multiplet in the aromatic region. The compound was oxidized by potassium dichromate to a sulphone considered to have structure 3.



Elemental analyses and mass spectrum were consistent with this structure. The NMR spectrum (in CF₃COOD) of the sulphone consisted of a singlet at δ 9.43 ppm in addition to a multiplet in the aromatic region (δ 8.11–9.01). The integral ratio of the singlet to that of the multiplet was 1:6 indicating that the singlet corresponded to two hydrogens. The singlet is assigned to the hydrogens

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in the 2 and 2' positions of 3 which are deshielded by the presence of the nitrogen and sulphone groups in *ortho* positions. The NMR spectrum of the sulphone fully confirms the proposed structures since other conceivable isomers, namely the corresponding 3,2', 3,4'- and 3,5'-sulphonyldipyridines would not contain such a deshielded singlet corresponding to two protons in their NMR spectrum. The singlet sometimes showed evidence of slight splitting ($J = 2$ Hz) presumably due to *meta* coupling.

The mechanism for the formation of 2 from the sodium salt of the bipyridyl-sulphonic acid is not yet clear but it is interesting to record that an analogy for this reaction was reported many years ago by STENHOUSE⁵ who obtained diphenyl sulphide from the distillation of sodium benzene-sulphonate.

Experimental

UV and NMR spectra were obtained as described previously⁴. Mass spectra were determined with an AEI MS30 spectrometer.

6,6'-Bis-(2-pyridyl)-3,3'-thiodipyridine (2)

The sodium salt of 2,2'-bipyridyl-5-sulphonic acid (5 g) was finely ground and heated in a porcelain boat in a silica tube. Nitrogen was passed over to flush out any product. At 500–600 °C a brown oil was carried over along with the nitrogen. It solidified on cooling. The temperature was maintained at 600 °C for 2 hours. The product was crystallized from dichloromethane/charcoal and then petroleum (b. p. 60–80 °C) to afford almost colourless needles, m. p. 124–126 °C (yield 20%).

C₂₀H₁₄N₄S (342)

Calcd C 70.1 H 4.1 N 16.4 S 9.4,
Found C 70.1 H 4.3 N 16.2 S 9.7.

NMR-spectrum (CDCl₃): $\delta = 7.15$ – 7.40 (m, 2 H), 7.65 – 7.95 (m, 4 H), 8.35 – 8.72 (m, 8 H) [ppm].

Mass-spectrum: $M^+ = 342$,

UV-spectrum (C₂H₅OH): λ_{\max} 242, 301,
(log ϵ 4.20, 4.37) [nm].

6,6'-Bis-(2-pyridyl)-3,3'-sulphonyldipyridine (3)

6,6'-Bis-(2-pyridyl)-3,3'-thiodipyridine (0.2 g) was dissolved in acetic acid (8 ml) and treated at 50 °C with a solution of potassium dichromate (0.43 g) in concentrated sulphuric acid (8 ml) and water (10 ml). After 2 hours the mixture was cooled and made strongly alkaline with sodium hydroxide solution. The precipitate was washed well with 10% sodium hydroxide solution and then water. It was crystallized from ethanol to afford colourless plates, m. p. 291–292 °C (dec.).

C₂₀H₁₄N₄O₂S (374)

Calcd C 64.2 H 3.75 N 15.0 S 8.6,
Found C 64.3 H 3.85 N 15.05 S 8.8.

NMR spectrum (CF_3COOD): $\delta = 8.11\text{--}9.01$
(m, 12 H), 9.43 (s, 2 H, 2,2'-aromatic H) [ppm].

Mass spectrum: $M^+ = 374$,

UV-spectrum ($\text{C}_2\text{H}_5\text{OH}$): λ_{max} . 243, 252 sh, 302,
(log ϵ 4.20, 4.19, 4.62) [nm].

¹ For example: H. KING and L. L. WARE, *J. Chem. Soc.* **1939**, 873; T. DEWING, W. H. GRAY, B. C. PLATT, and D. STEPHENSON, *J. Chem. Soc.* **1942**, 239; S. KRUGER and F. G. MANN, *J. Chem. Soc.* **1955**, 2755; D. JERCHEL, H. FISCHER, and K. THOMAS, *Chem. Ber.* **89**, 2921 [1956]; J. RENAULT, *Ann. Chim. Paris* **10**, 135 [1955].

² A. SENNING, *Acta Chem. Scand.* **18**, 269 [1964].

³ T. TALIK and Z. TALIK, *Roczniki Chem.* **40**, 1675 [1966].

⁴ N. H. PIRZADA, P. M. POJER, and L. A. SUMMERS, *Z. Naturforsch.* **31b** [1976].

⁵ J. STENHOUSE, *Proc. Royal Soc. London* **14**, 353 [1865].