

## Isolation and X-Ray Crystal Structure of a Novel Dihydroterpyridine Dimer formed *via* an Anionic [6 + 4] Cycloaddition

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**Summary** The identity of a novel dimer (**2**), isolated as a by-product from the reaction of 2-lithiopyridine with 2,2'-bipyridine, has been assigned on the basis of X-ray crystal structure analysis.

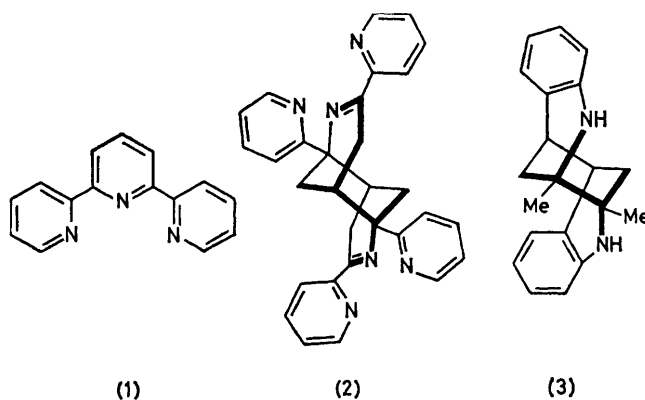
In order to synthesize a series of halogenated polypyridines to be used in the preparation of macrocyclic crown ethers containing heterocyclic rings,<sup>1,2</sup> a convenient route to substituted 2,2':6',2''-terpyridines was required. 2,2'-Bipyridine upon treatment with 2-lithiopyridine in diethyl ether at -40 °C gave (35%) the expected terpyridine (**1**)<sup>3</sup> as well as an unexpected (5%) high-melting solid† (**2**) (m.p. 267–268 °C), which readily precipitated after hydrolysis of the reaction mixture. The complexity of the 200 MHz <sup>1</sup>H n.m.r. spectrum of (**2**) precluded structure elucidation by simple spectral analysis,‡ and so an X-ray crystal structure determination of (**2**) was undertaken. Recrystallization from ether-acetic acid (2:1) resulted in the incorporation of two equiv. of acetic acid per equiv. of (**2**).

**Crystal data:** § C<sub>34</sub>H<sub>34</sub>N<sub>6</sub>O<sub>4</sub>, monoclinic, space group P2<sub>1</sub>/n, *a* = 10.946(2), *b* = 9.674(3), *c* = 14.052(3) Å, β = 97.89(2)°, *Z* = 2, *D*<sub>c</sub> = 1.331 g cm<sup>-3</sup>, *R* = 0.031 for 1135 observed data having *F*<sub>0</sub> > 2σ(*F*<sub>0</sub>) and 2 < θ < 22°.

† Analytical data (±0.2%) were in accord with the assigned structure.

‡ Spectral data: 200 MHz <sup>1</sup>H n.m.r. (CDCl<sub>3</sub> with 1% Me<sub>4</sub>Si) δ 1.79 (m, 2H), 2.85 (m, 4H), 2.98 (m, 4H), 7.22 (ddd, *J* 8.0, 6.4, and 1.2 Hz, 2H), 7.27 (ddd, *J* 8.0, 6.4, and 1.2 Hz, 2H), 7.71 (ddd, *J* 8.0, 8.0, and 1.2 Hz, 2H), 7.77 (ddd, *J* 8.0, 8.0, and 1.2 Hz, 2H), 8.17 (dd, *J* 8.0 and 1.2 Hz, 2H), 8.28 (dd, *J* 8.0 and 1.2 Hz, 2H), 8.52 (dd, *J* 6.4 and 1.2 Hz, 2H), and 8.57 (dd, *J* 6.4 and 1.2 Hz, 2H); i.r.(KBr) 1638 (C=N) cm<sup>-1</sup>; m.s. *m/e* 470 (*M*<sup>+</sup>, 0.03%), 236 (51.1), and 234 (100).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23124 (6 pp) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index Issues.



λ = 0.71073 Å for Mo-K<sub>α</sub> radiation. Intensity data were collected by the θ-2θ scan method (Enraf-Nonius CAD4 diffractometer) using a crystal sealed in a thin-walled glass capillary to prevent solvent loss. The structure was solved by direct methods and refined by full-matrix least-squares, treating non-hydrogen atoms anisotropically. Hydrogen atom positions were located from difference maps and their isotropic temperature factors were refined.

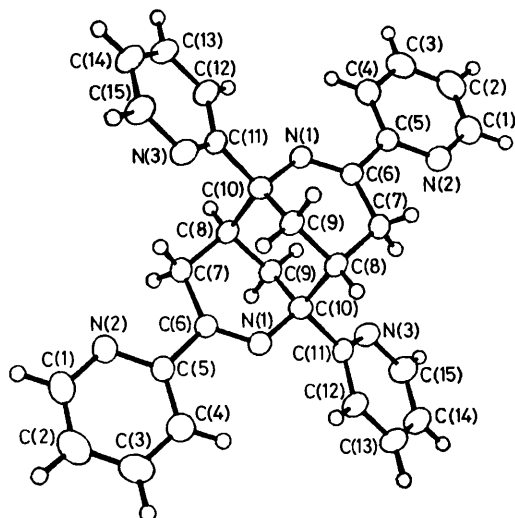
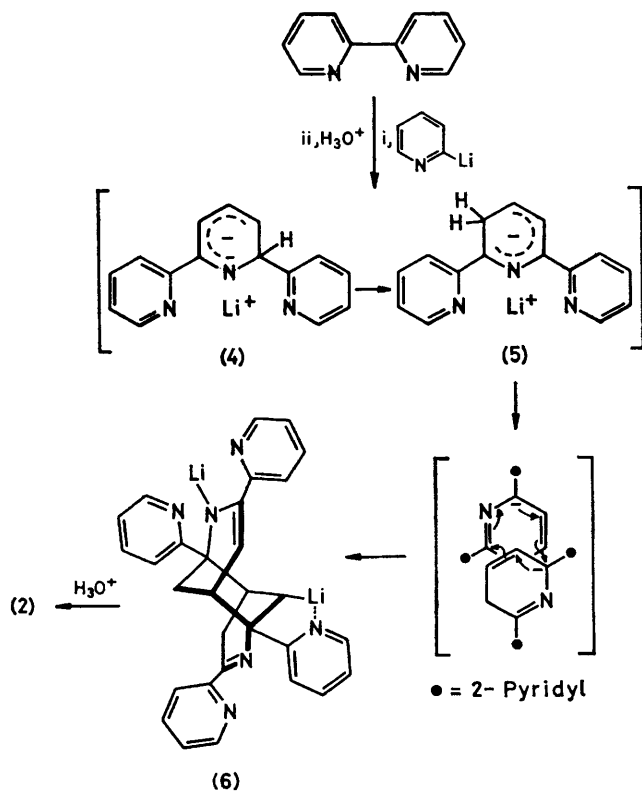


FIGURE. Structure of the dimer (2). Distances and angles within the central ring system are: N(1)-C(6) 1.273(2), N(1)-C(10) 1.479(3), C(6)-C(5) 1.500(3), C(6)-C(7) 1.503(3), C(7)-C(8) 1.534(3), C(8)-C(9) 1.526(3), C(9)-C(10) 1.519(3), C(10)-C(8) 1.567(3), C(10)-C(11) 1.538(3) Å; C(6)-N(1)-C(10) 119.8(2), N(1)-C(6)-C(5) 116.2(2), N(1)-C(6)-C(7) 126.6(2), C(5)-C(6)-C(7) 117.3(2), C(6)-C(7)-C(8) 112.9(2), C(7)-C(8)-C(9) 107.2(2), C(7)-C(8)-C(10) 113.2(2), C(9)-C(8)-C(10) 110.2(2), C(8)-C(9)-C(10) 108.5(2), N(1)-C(10)-C(9) 111.0(2), N(1)-C(10)-C(11) 105.5(2), N(1)-C(10)-C(8) 107.0(2)°.

The Figure illustrates the unexpected bridging exhibited by the dimer (2) and also the chair conformation of the central ring. Hydrogen bonds are formed from the acetic acid molecules to the most basic nitrogen atoms [N(3)] and are essentially linear, having an O...N distance of 2.727(3) Å, an H...N distance of 1.571 Å, and an O-H...N angle of 174°. The surprising feature of this condensation dimer is the mode of dimerization, in which there is a symmetrical linkage of the two dihydroterpyridine units. To the best of our knowledge, this is the first example of a 2,4':2',4-linked dimer involving a reduced pyridine species; however, Heller's dimer<sup>4-6</sup> (3) has been demonstrated to possess a closely related structure, but with a 2,2':4,4'-linkage.

Formation of (2) can be envisaged as occurring by an initial  $\alpha$ -addition of 2-lithiopyridine to 2,2'-bipyridine to produce the anion (4), which undergoes a thermally allowed [1s,4s] sigmatropic shift to give the anion (5) (Scheme).



SCHEME

The electron-withdrawing effect of the 2-pyridyl moieties in (5) results in enhanced anion stabilization [over that in (4)]. Subsequently, (5) can dimerize *via* a [6 + 4] cycloaddition to generate the stable dianion (6). Normal anion-anion repulsion, which would hinder such a mode of cyclization, is minimized by formation of covalent lithium-carbon bonds in which the metal ions can be stabilized by the co-ordination of the metal to the nitrogen atoms of the juxtaposed 2-pyridyl groups. Hydrolysis of (6) gives rise to the observed dimer (2).

We thank Professor K. N. Houk for his timely comments and the National Science Foundation for its financial support.

(Received, 29th April 1981; Com. 512.)

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