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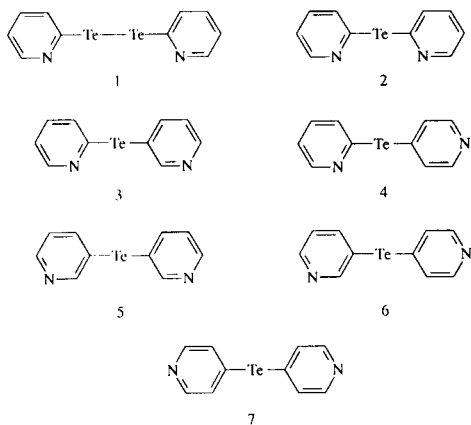
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All six isomers of tellurobispyridine, namely 2,2'-tellurobispyridine, 2,3'-tellurobispyridine, 2,4'-tellurobispyridine, 3,3'-tellurobispyridine, 3,4'-tellurobispyridine and 4,4'-tellurobispyridine have been synthesised.

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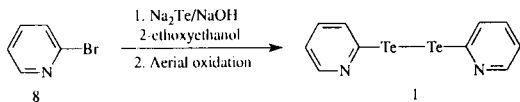
No tellurobispyridine has so far been reported although 2,2'-ditellurobispyridine (**1**) [1-3] has been investigated and other ditellurobispyridines are mentioned in a patent although no syntheses were given [4]. In continuation of our studies of the chemistry and properties of oxybispyridines [5-7], thiobispyridines [5,8] and selenobispyridines [5,9] we now report the synthesis of all six tellurobispyridines, namely 2,2'-tellurobispyridine (**2**), 2,3'-tellurobispyridine (**3**), 2,4'-tellurobispyridine (**4**), 3,3'-tellurobispyridine (**5**), 3,4'-tellurobispyridine (**6**) and 4,4'-tellurobispyridine (**7**).

Block 1



The starting material for the synthesis of 2,2'-tellurobispyridine (**2**) was 2,2'-ditellurobispyridine (**1**) which was prepared by the new route of reacting 2-bromopyridine (**8**) with tellurium and sodium borohydride in alkaline 2-ethoxyethanol followed by aerial oxidation. 2,2'-Tellurobispyridine

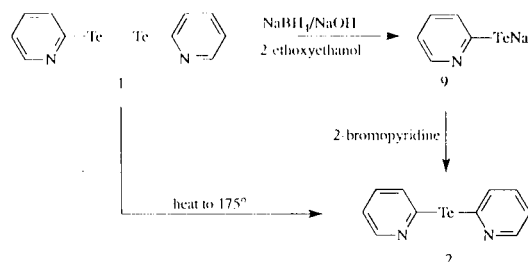
Block 2



(**2**) was then obtained from 2,2'-ditellurobispyridine (**1**) either by reductively splitting the Te-Te bond with alkaline sodium borohydride followed by reaction of the resultant sodium 2-pyridyltellurolate (**9**) with 2-bromopyridine or simply by heating 2,2'-ditellurobispyridine (**1**) to

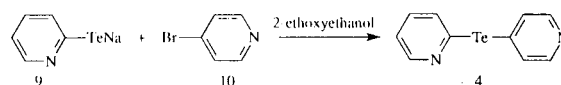
175° whereby one tellurium atom was extruded affording 2,2'-tellurobispyridine (**2**).

Block 3



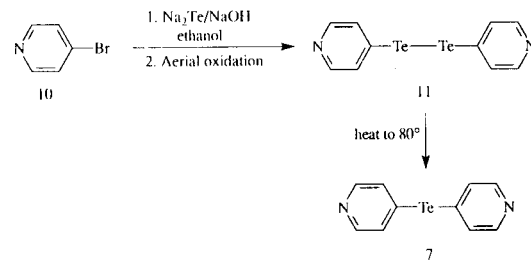
2,4'-Tellurobispyridine (**4**) was prepared from 2,2'-ditellurobispyridine (**1**) in a similar way by reacting the intermediate sodium 2-pyridyltellurolate (**9**) with 4-bromopyridine (**10**).

Block 4



4,4'-Ditellurobispyridine (**11**) was prepared by an analogous route to that 2,2'-ditellurobispyridine (**1**) by reacting 4-bromopyridine (**10**) with tellurium and sodium borohydride in alkaline ethanol followed by aerial oxidation. 4,4'-Ditellurobispyridine (**11**) readily lost one tellurium atom on heating to afford 4,4'-tellurobispyridine (**7**).

Block 5

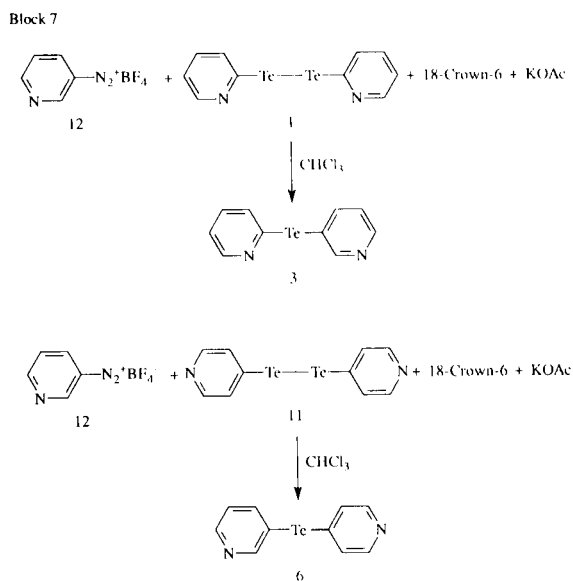


An adaptation of the method due to Engman [10] was used for the preparation of 3,3'-tellurobispyridine (**5**). 3-Aminopyridine was diazotised with fluoroboric acid and the resultant 3-pyridyldiazonium tetrafluoroborate (**12**)

was reacted with a cold solution of potassium tellurocyanate in dimethyl sulfoxide under a nitrogen atmosphere to afford 3,3'-tellurobispyridine (**5**).



2,3'-Tellurobispyridine (**3**) and 3,4'-tellurobispyridine (**6**) were prepared using an adaptation of the method due to Luxen and Christiaens [11]. The reaction of 3-pyridyldiazonium tetrafluoroborate with 2,2'-ditellurobispyridine (**1**) and 4,4'-ditellurobispyridine (**11**) respectively in chloroform in the presence of potassium acetate and a catalytic amount of the phase transfer agent, 18-crown-6, led to the formation of 2,3'-tellurobispyridine (**3**) and 3,4'-tellurobispyridine (**6**) in good yields. The crown ether increases the nucleophilicity of the acetate ion which attacks the tetrafluoroborate salt to initiate a chain of reactions leading to the formation of a 3-pyridyl radical which attacks the weak Te-Te bond of the ditelluride to form the respective unsymmetrical monotelluride.



All the tellurobispyridines gave satisfactory elemental analyses and nmr spectra. In the electron mass spectra, the molecular ion was not the base peak with any of the six tellurobispyridines, a situation analogous to that observed with the selenobispyridines [9]. The molecular ion at mass 286 gave a peak of 30-70% of the intensity of the base peak which was due to the $\text{C}_5\text{H}_4\text{N}^+$ ion at mass 78 for 2,2'- and 2,3'-tellurobispyridines and to the C_4H_3^+ ion at mass 51 for the other four isomers. One of the major fragmentation routes from the molecular ion in all six cases involved loss of tellurium from the molecular ion or the M-1 ion to afford bipyridine species.

EXPERIMENTAL

The nmr spectra refer to ^1H spectra run in deuteriochloroform with tetramethylsilane as internal standard and ^{125}Te spectra run in carbon tetrachloride with dimethyl telluride as external reference. Ultraviolet absorption spectra were taken in ethanol solution.

2,2'-Ditellurobispyridine (**1**).

Tellurium powder (2.55 g) and sodium borohydride (4 g) were slurried in a solution of sodium hydroxide (2.0 g) in 2-ethoxyethanol (200 ml) under a nitrogen atmosphere. The mixture was refluxed for 2 hours by which time the solution was colourless. 2-Bromopyridine (10.0 g) was added and the solution refluxed for 90 minutes. After cooling, the solution was stirred in air for 1 hour and then poured into an aqueous potassium carbonate solution (0.5M, 400 ml). This solution was then extracted with chloroform (5 x 200 ml). The extracts were dried over magnesium sulfate, filtered and the solvent removed under pressure to afford a brown oil, which solidified on standing. The crude solid was recrystallised from hexane to afford 2,2'-ditellurobispyridine as blood-red crystals, mp 52° (2.3 g). Literature [1-3] mps range from $50-52^\circ$. The ^1H nmr spectrum consisted of a doublet at δ 8.40-8.45 (2H, 6,6' protons), a doublet at 7.98-8.06 (2H, 3,3' protons), a multiplet at 7.27-7.44 (2H, 4,4' protons) and a multiplet at 6.93-7.06 ppm (2H, 5,5' protons). The ^{125}Te spectrum gave a signal at δ 502 ppm. The uv spectrum showed λ max 228 (sh), 260, 289 (sh), 389 nm ($\log \epsilon$ 4.23, 4.07, 3.88 and 2.96).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{Te}_2$: C, 29.2; H, 2.0; N, 6.8. Found: C, 29.0; H, 1.8; N, 6.5.

2,2'-Tellurobispyridine (**2**).

(a) 2,2'-Ditellurobispyridine (2.0 g) and sodium hydroxide (0.5 g) were dissolved in 2-ethoxyethanol (100 ml) under nitrogen. Sodium borohydride (2.0 g) was added and the solution refluxed for 1 hour. After cooling, 2-bromopyridine (1.6 g) was added and the mixture refluxed for 3 hours. The solution was poured into chloroform (300 ml). The chloroform layer was washed with an aqueous sodium hydroxide solution (1M, 5 x 100 ml), dried over magnesium sulfate and then evaporated under reduced pressure to yield an orange oil. The oil was chromatographed on a column packed with alumina. On elution with hexane, the first yellow fraction was collected and the solvent removed. The residue was distilled at reduced pressure to afford 2,2'-tellurobispyridine as a pale yellow oil, bp $143^\circ/0.25$ mm (yield 2.29 g). The ^1H nmr spectrum consisted of a doublet at δ 8.50-8.58 (2H, 6,6' protons), a doublet at 7.68-7.79 (2H, 3,3' protons), a multiplet at 7.33-7.53 (2H, 4,4' protons) and a multiplet at 7.04-7.20 ppm (2H, 5,5' protons). The ^{125}Te spectrum gave a signal at δ 793 ppm. The uv spectrum showed λ max 216, 253, 307 and 337 nm ($\log \epsilon$ 4.23, 3.99, 3.82 and 3.46). The mass spectrum showed peaks above 10% intensity of base peak at 286 (M^+ , 51), 285 (36), 284 (47), 283 (35), 282 (30), 281 (28), 280 (13), 156 (10), 155 (17), 130 (10), 78 (100), 52 (13), 51 (77).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{Te}$: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.6; H, 2.6; N, 9.7.

(b) 2,2'-Ditellurobispyridine (0.5 g) was dissolved in methanol (10 ml) and the solution heated on an oil bath until the methanol had evaporated. The oil bath temperature was increased to 170° at which stage tellurium precipitated. Heating was continued for 1 hour. After cooling, the residue was dissolved in methanol (50 ml) and filtered to remove the precipitated tellurium. The meth-

anol extract was evaporated and the brown oil distilled under reduced pressure to afford 2,2'-tellurobispyridine identical to that formed in method (a), yield 0.23 g.

2,4'-Tellurobispyridine (4).

2,2'-Ditellurobispyridine (0.5 g) and sodium hydroxide (0.1 g) were dissolved in 2-ethoxyethanol (50 ml) under a nitrogen atmosphere. Sodium borohydride (0.5 g) was added and the solution refluxed for 1 hour. After cooling, 4-bromopyridine hydrochloride (0.6 g) was added and the mixture refluxed for a further 5 hours. The solution was poured into chloroform (200 ml) and then washed with an aqueous sodium hydroxide solution (1M, 5 x 100 ml). The chloroform extract was dried over magnesium sulfate and then evaporated under reduced pressure to yield a red oil which was chromatographed on a column packed with alumina. On elution with carbon tetrachloride the major fraction was collected and the solvent removed. The residue was distilled under pressure to afford 2,4'-tellurobispyridine as an orange oil, bp 156°/0.55 mm (yield 0.50 g). The ¹H nmr spectrum consisted of a doublet at δ 8.53-8.60 (1H, 6 proton), a doublet at 8.38-8.46 (2H, 2',6' protons), a multiplet at 7.33-7.69 (4H, 3,3',4,5' protons) and a multiplet at 7.08-7.23 ppm (1H, 5 proton). The ¹²⁵Te spectrum gave a signal at δ 750 ppm. The uv spectrum showed λ max 216, 230 sh, 255, 301 and 338 sh nm (log ε 4.15, 4.03, 3.87, 3.83 and 3.37). The mass spectrum showed peaks above 10% intensity of base peak at 286 (M⁺, 60), 285 (28), 284 (56), 283 (25), 282 (33), 281 (25), 280 (13), 156 (18), 155 (16), 79 (15), 78 (88), 52 (12), 51 (100).

Anal. Calcd. for C₁₀H₈N₂Te: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.6; H, 2.9; N, 9.7.

4,4'-Ditellurobispyridine (11).

Tellurium powder (2.55 g) and sodium borohydride (5 g) were slurried in a solution of sodium hydroxide (0.8 g) in ethanol (200 ml) in a nitrogen atmosphere. The mixture was refluxed for 1 hour to obtain a colorless solution. After cooling, 4-bromopyridine hydrochloride (7.8 g) was added and the solution refluxed for 24 hours. After cooling the solution was stirred in air for 1 hour and then poured into an aqueous potassium carbonate solution (0.5M, 400 ml). This solution was extracted with chloroform (5 x 100 ml). The extracts were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure to afford a red-brown solid. The crude solid was extracted with hot hexane (2 x 50 ml) to remove any 4,4'-tellurobispyridine. The residue was recrystallised from methanol to afford 4,4'-ditellurobispyridine as blood-red crystals, mp 96° (yield 3.4 g). The ¹H nmr spectrum consisted of a doublet at δ 8.29-8.36 (4H, 2,2',6,6' protons) and a doublet at 7.62-7.69 ppm (4H, 3,3',5,5' protons). The ¹²⁵Te spectrum gave a signal at δ 483 ppm. The uv spectrum showed λ max 247, 264 and 345 nm (log ε 4.14, 4.07 and 3.70).

Anal. Calcd. for C₁₀H₈N₂Te₂: C, 29.2; H, 2.0; N, 6.8. Found: C, 29.1; H, 1.9; N, 6.7.

4,4'-Tellurobispyridine (7).

4,4'-Ditellurobispyridine (0.5 g) was dissolved in methanol (10 ml) and the solution heated on a steam bath. The mixture was allowed to boil to dryness and heating was continued for 1 hour. The residue was dissolved in methanol (20 ml) and filtered to remove the precipitated tellurium. The methanol extract was evaporated under reduced pressure to yield a yellow-green oil, which solidified upon standing. The crude solid was recrystallised from

hexane to afford 4,4'-tellurobispyridine as colourless needles, mp 121° (yield 0.32 g). The ¹H nmr spectrum consisted of a doublet at δ 8.39-8.46 (4H, 2,2',6,6' protons) and a doublet at 7.50-7.57 ppm (4H, 3,3',5,5' protons). The ¹²⁵Te spectrum gave a signal at δ 708 ppm. The uv spectrum showed λ max 213, 247, 263, 300 and 333 nm (log ε 4.26, 3.81, 3.85, 3.89 and 3.46). The mass spectrum showed peaks above 10% intensity of base intensity at 286 (M⁺, 71), 285 (11), 284 (64), 282 (43), 281 (18), 280 (12), 208 (13), 206 (13), 204 (10), 156 (57), 155 (21), 130 (10), 79 (25), 78 (83), 52 (12), 51 (100).

Anal. Calcd. for C₁₀H₈N₂Te: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.4; H, 2.9; N, 9.6.

3,3'-Tellurobispyridine (5).

Pyridine-3-diazonium tetrafluoroborate (2.4 g) was added rapidly to an ice-cold suspension of potassium tellurocyanate, prepared by heating tellurium powder (1.60 g) and potassium cyanide (0.82 g) in DMSO at 100° [12] under a nitrogen atmosphere. When the initial vigorous reaction had subsided, the ice bath was removed and the stirring continued at ambient temperature for 2 hours. The mixture was dissolved in chloroform (200 ml), filtered and then washed with an aqueous sodium hydroxide solution (1M, 5 x 50 ml). The chloroform extract was dried over magnesium sulfate and then evaporated under reduced pressure to yield a yellow-brown oil. The crude oil was chromatographed on a column packed with alumina. On elution with carbon tetrachloride, the pale yellow fraction was collected and the solvent removed. The residue was distilled under reduced pressure to afford 3,3'-tellurobispyridine as a pale yellow oil, bp 128-132°/0.35 mm, which solidified on standing, mp 36° (1.3 g). The ¹H nmr spectrum consisted of a singlet at δ 8.87 (2H, 2,2' protons), a multiplet at 8.49-8.56 (2H, 6,6' protons), a multiplet at 7.93-8.06 (2H, 4,4' protons) and a multiplet at 7.09-7.22 ppm (2H, 5,5' protons). The ¹²⁵Te spectrum gave a signal at δ 604 ppm. The uv spectrum showed λ max 215, 249 and 289 nm (log ε 4.32, 3.91 and 3.69). The mass spectrum showed peaks above 10% intensity of base peak at 286 (M⁺, 31), 284 (29), 282 (18), 156 (59), 155 (23), 129 (17), 78 (58), 51 (100).

Anal. Calcd. for C₁₀H₈N₂Te: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.5; H, 2.9; N, 9.6.

2,3'-Tellurobispyridine (3).

Pyridine-3-diazonium tetrafluoroborate (2 g) was slurried in an ice-cold chloroform solution (10 ml) containing 18-crown-6 (10 mg) and 2,2'-ditellurobispyridine (1.54 g) under a nitrogen atmosphere. The vessel was protected from light and then potassium acetate (0.5 g) was added. The mixture was stirred for 30 minutes at 0° and then allowed to come to ambient temperature over 2 hours. The clear orange solution was filtered and the solvent removed under reduced pressure. The crude orange oil was chromatographed on a column packed with alumina. On elution with carbon tetrachloride the first yellow fraction was collected and the solvent removed. The residue was distilled under reduced pressure to yield 2,3'-tellurobispyridine as a pale yellow oil, bp 141°/0.28 mm (yield 1.2 g). The ¹H nmr spectrum consisted of a singlet at δ 9.03 (1H, 2' proton), a multiplet at 8.41-8.62 (2H, 6,6' protons), a doublet at 8.17-8.26 (1H, 4' proton), a doublet at 7.67-7.76 (1H, 3 proton), and a multiplet at 7.02-7.49 (3H, 4,5,5' protons). The ¹²⁵Te spectrum gave a signal at δ 700 ppm. The uv spectrum showed λ max 220, 228, 253 and 305 nm (log ε 4.05, 4.02, 3.93 and 3.72). The mass spectrum showed peaks above

10% intensity of base peak at 286 (M^+ , 55), 285 (65), 284 (52), 283 (58), 282 (29), 281 (42), 280 (20), 156 (16), 155 (22), 130 (11), 79 (15), 78 (100), 57 (13), 52 (20), 51 (88).

Anal. Calcd. for $C_{10}H_8N_2Te$: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.6; H, 2.9; N, 10.1.

3,4'-Tellurobispyridine (6).

Pyridine-3-diazonium tetrafluoroborate (2 g) was slurried in an ice-cold chloroform solution (10 ml) containing 18-crown-6 (10 mg) and 4,4'-ditellurobispyridine (1.54 g) under a nitrogen atmosphere. The vessel was protected from light and then potassium acetate (0.5 g) was added. The mixture was stirred for 30 minutes at 0° and then allowed to come to ambient temperature over 2 hours. The clear orange solution was filtered and the solvent removed under reduced pressure. The crude orange oil was chromatographed on a column packed with alumina. On elution with carbon tetrachloride, the first yellow fraction was collected and the solvent removed. The residue was crystallised from hexane to yield 3,4'-tellurobispyridine as colourless crystals, mp 58° (yield 1.4 g). The 1H nmr spectrum consisted of a singlet at δ 8.88 (1H, 2 proton), a multiplet at 8.39-8.55 (3H, 2',6,6' protons), a multiplet at 7.95-8.10 (1H, 4 proton), a multiplet at 7.50-7.57 (2H, 3',5' protons) and a multiplet at 7.11-7.25 ppm (1H, 5 proton). The ^{125}Te spectrum gave a signal at δ 657 ppm. The uv spectrum showed λ max 212, 259 and 298 nm ($\log \epsilon$ 4.27, 3.85 and 3.98). The mass spectrum showed peaks above 10% intensity of base peak at 286 (M^+ , 41), 284 (38), 282 (23), 207 (11), 156 (38), 79 (19), 78 (56), 51 (100).

Anal. Calcd. for $C_{10}H_8N_2Te$: C, 42.3; H, 2.8; N, 9.9. Found: C, 42.0; H, 2.9; N, 9.6.

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