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Received January 20, 1995

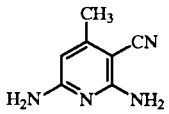
2,6-Dihydroxy-4-methyl-3-pyridinecarbonitrile is converted *via* its 2,6-dichloro analog into the corresponding 2-amino-6-chloro, 2-chloro-6-amino, and 2,6-diamino derivatives. The last reacts with benzenesulfonyl chloride to yield a tris-sulfonyl derivative, the structure of which is demonstrated by X-ray analysis.

J. Heterocyclic Chem., **32**, 979 (1995).

Introduction.

Aryl diazonium salts couple at the 5-position with 2,6-diamino-4-methyl-3-pyridinecarbonitrile (**1**) and its *N*-alkylamino and *N*-arylamino derivatives. The resulting azo dyes have found application in the dyeing of polyester and acrylic fibers [1-2], textile materials containing cellulose [3], polyamide, polyester and cellulose ester fibers [4] and PVC [5]. In general, 2,6-diamino-4-methyl-3-cyanopyridine **1** and its derivatives are prepared by condensation of 2,6-dichloro-4-methyl-3-pyridinecarbonitrile (**2**) with amines. It has been reported that carrying out the condensation under mild conditions allows stepwise substitution of the chlorine atoms with two different amino or substituted amino groups [6-8].

Block 1



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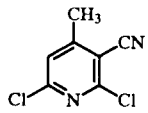


2

Despite the great synthetic importance of diamine **1** and its substituted derivatives, relatively little information is found in the literature on their reactivity. We now report a study on the synthesis and reactions of 2,6-diamino-4-methyl-3-pyridinecarbonitrile (**1**).

Result and Discussion.

Parent Pyridine System.

According to the literature [9], cyclocondensation of ethyl acetoacetate (**3**) with cyanoacetamide is catalyzed by base (*e.g.* potassium hydroxide or piperidine) to give 2,6-dihydroxy-4-methyl-3-pyridinecarbonitrile (**6**) in good yield (Scheme 1). A modification of the above procedure is now reported involving direct conversion without separation of the potassium salt of **6** by acidification

Scheme 1

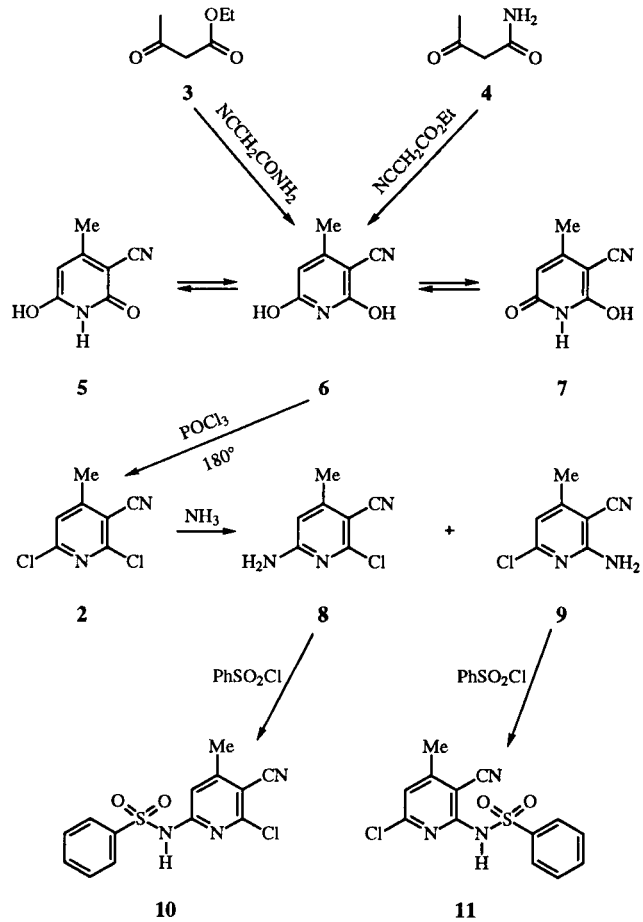


Table 1

^{1}H NMR Data [a] of the 3-Pyrrolinecarbonitriles Prepared

Number	H-5	Me	Other Substituents
1	5.74 (s)	2.19 (s)	5.88 (bs, 2H), 5.99 (bs, 2H)
2	7.30 (q, J = 0.7 Hz)	2.60 (d, J = 0.7 Hz)	
6	5.61	2.27 (s)	8.40 (bs, 2H)
8	6.33 (s)	2.29 (s)	7.39 (bs, 2H)
9	6.68 (s)	2.32 (s)	7.29 (bs, 2H)
10	7.00 (s)	2.44 (s)	7.66 (m, 3H), 8.05 (d, J = 7.7 Hz, 2H)
11	7.12 (q, J = 0.7 Hz)	2.45 (d, J = 0.7 Hz)	7.56 (m, 3H), 8.06 (m, 2H)
12	—	2.38 (s)	6.47 (bs, 2H), 6.54 (bs, 2H), 7.01 (d, J = 7.3 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 7.4 Hz, 2H)
13	5.93 (s)	2.25 (s)	2.70-5.30 (bs, 2H), 7.34 (m, 3H), 7.63 (m, 2H), 7.64-8.30 (bs, 3H)
14	6.20 (s)	2.23 (s)	6.38 (bs, 2H), 7.51 (m, 3H), 8.02 (d, J = 7.1 Hz, 2H), 11.15 (bs, 1H)
16	7.07 (s)	2.47 (s)	7.41 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 6.8 Hz, 1H), 7.60 (t, J = 8.0 Hz, 4H), 7.72 (t, J = 6.8 Hz, 2H), 7.84 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 8.1 Hz, 4H), 11.6 (bs, 1H)
17	7.12 (s)	2.48 (s)	7.33 (m, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 8.0 Hz, 4H), 7.74 (m, 3H), 7.84 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.4 Hz, 4H), 8.57 (bd, J = 3.2 Hz, 2H)

[a] Nmr spectra taken in DMSO-d_6, except for compound **2**, where deuteriochloroform was used as the solvent.

with hydrochloric acid. This procedure results in a 65% yield of **6**. The alternative condensation of acetoacetamide (**4**) and ethyl cyanoacetate gave **6** in only 25% yield, which increased to 46% when sodium ethoxide was used as the base. However the route from acetoacetamide is less attractive because amide **4** reacts with ethyl cyanoacetate less readily than does acetoacetate **3** with cyanoacetamide.

Aminochloropyridines.

The reaction of **6** with phosphorus oxychloride as per [9] at 200° in a steel autoclave gave dichloropyridine **2** in 98% yield (Scheme 1), while no **2** was produced when **6** was refluxed in phosphorus oxychloride (bp 106°) for 48 hours. Reaction of **2** with liquid ammonia at 20°, under pressure, gave a mixture of the 2-chloro-6-amino- (**8**, with a characteristic singlet for the H-5 resonance at δ 6.35) and 6-chloro-2-amino- (**9**, H-5 resonance at δ 6.53) derivatives in a ratio of 73:27. Increasing the reaction temperature to 50° changed the ratio between the isomers **8** and **9** to 64:36. When a saturated solution of ammonia in methanol at 20° under atmospheric pressure was used in this reaction, a complex mixture resulted. The nmr spectra of this mixture showed partial substitution of the chlorine atoms by methoxy groups. These results contrast with reports in patents which claim (i) that substitution of the

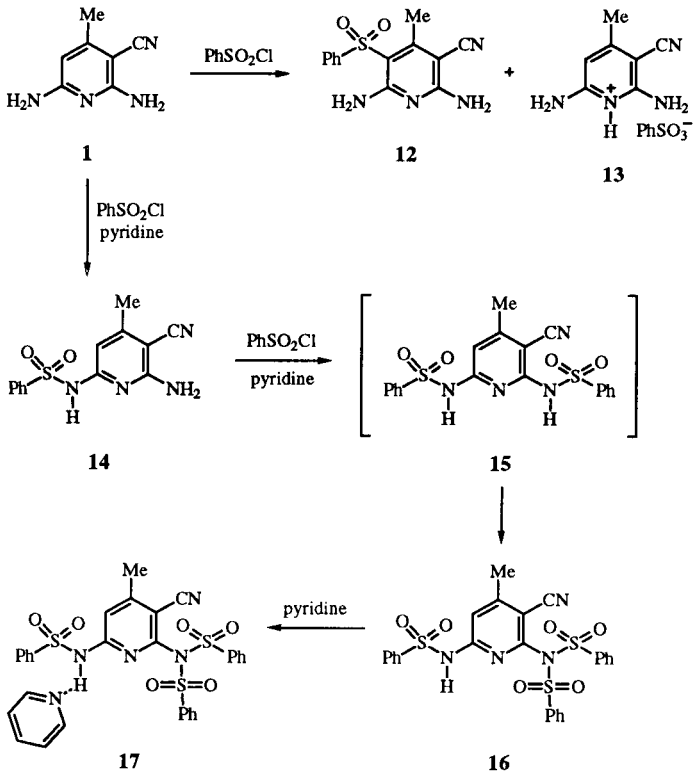
Table 2

^{13}C NMR Data [a] of the 3-Pyridinecarbonitriles Obtained

Number	C-2	C-3	C-4	C-5	C-6	CN	Me	Other
1	160.6	77.9	151.6	98.8	161.1	118.5	20.0	—
2	152.6	110.3	156.5	124.1	153.7	113.3	20.7	—
6	162.2	89.8	160.0	93.4	170.0	116.7	20.8	—
8	152.1	95.1	152.7	106.6	160.9	116.1	20.0	—
9	160.2	88.9	156.0	112.2	152.8	115.5	19.7	—
10	152.9	103.8	156.3	110.2	150.8	114.4	20.5	127.6 (2 C), 129.2 (2 C), 133.7, 139.2
11	151.4	98.3	157.4	120.0	152.3	113.9	20.0	127.9 (2 C), 128.7 (2 C), 133.2, 140.2
12	160.7	81.8	157.9	95.6	162.0	117.6	19.6	125.1 (3 C), 129.0 (2 C), 136.4
13	153.7 [b]	140.0	157.7	98.5	153.8 [b]	114.6	21.0	125.6 (2 C), 127.9 (2 C), 129.4, 146.1
14	158.8	83.1	154.0	100.8	153.2	116.2	20.2	127.4 (2 C), 128.5 (2 C), 132.4, 140.5
16	148.6	107.3	154.8	113.4	153.2	113.7	20.6	127.7 (2 C), 128.9 (2 C), 129.0 (4 C), 129.1 (4 C), 133.0, 134.3 (2 C), 138.8 (2 C), 139.3
17	149.2	107.2	154.9	113.4	153.4	113.5	20.4	123.7, 127.4 (2 C), 128.8 (2 C), 128.9 (2 C), 129.0 (4 C), 133.0, 134.4 (2 C), 135.9, 138.5 (2 C), 139.3, 148.6

[a] Nmr spectra taken in DMSO-d_6, except for compound **2**, where deuteriochloroform was used as the solvent. [b] The assignment can be reversed.

Scheme 2



chlorine atom initially occurs predominantly at C-2 and (ii) that methanol is a good medium for the reaction of dichloropyridine **2** with amines [6,8].

Our literature search indicated that the minor isomer, chloroamine **9**, has not previously been reported and the main product, chloroamine **8**, was mentioned only in patents [10-11]. While fractional recrystallization failed to separate chloroamines **8** and **9**, analytical samples of each were obtained by column chromatography on silica gel using a dilute solution because of low solubility in chloroform. The significantly greater polarity of **8** as compared to **9** results from location of the opposing inductive effect of the CN and NH_2 groups on the same (**9**) or the opposite (**8**) side of the molecule and is in agreement with the structural assignments of **8** and **9** made on the basis of their nmr spectra.

The mixture of **8** and **9** was reacted with a limited amount of benzenesulfonyl chloride under basic conditions; unreacted **9** was easy to separate from the more soluble product sulfonamide **10** by recrystallization allowing collection of substantial amounts of the minor chloroamine isomer **9**. The lower reactivity of **9** probably reflects both a steric effect and an electronic effect of the cyano group which renders the amino group of **9** less nucleophilic than the amino group of **8**. The upfield shift of the cyano carbon resonance of **9** in relation to **8** (Table 2) provides additional support for this conclusion. Mixed chloroamines **8** and **9** were reacted with sodium hydride and benzenesulfonyl chloride in dimethyl sulfoxide to give a mixture of sulfonamides **10** and **11** (total yield 50%) which were easily separated by fractional recrystallization.

Table 3

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^3)

Atom	x	y	z	U_{eq} [a]
S(2)	1889(1)	3573(1)	3905(1)	17(1)
S(3)	4397(1)	2404(1)	4457(1)	16(1)
S(6)	708(1)	-1046(1)	8146(1)	18(1)
O(21)	2087(2)	4465(1)	4529(1)	24(1)
O(22)	684(1)	3087(1)	3982(1)	23(1)
O(31)	5071(1)	1244(1)	4323(1)	22(1)
O(32)	4762(1)	3529(1)	3813(1)	20(1)
O(61)	-173(1)	-563(2)	8918(1)	26(1)
O(62)	480(2)	-2159(1)	7794(1)	25(1)
N(2)	2899(2)	2273(2)	4196(1)	15(1)
N(6)	796(2)	83(2)	7152(1)	18(1)
N(1)	1841(2)	1083(2)	5661(1)	15(1)
C(2)	2330(2)	1133(2)	4675(2)	15(1)
C(3)	2357(2)	174(2)	4106(2)	16(1)
C(3A)	2820(2)	320(2)	3019(2)	19(1)
N(3A)	3145(2)	402(2)	2142(1)	28(1)
C(4)	1876(2)	-947(2)	4615(2)	17(1)
C(4A)	1900(2)	-2033(2)	4054(2)	24(1)
C(5)	1373(2)	-1012(2)	5648(2)	17(1)
C(6)	1362(2)	21(2)	6140(2)	15(1)
C(21)	2383(2)	4138(2)	2585(2)	20(1)
C(22)	2908(2)	5265(2)	2337(2)	33(1)
C(23)	3247(3)	5721(3)	1291(2)	47(1)
C(24)	3081(2)	5051(3)	528(2)	44(1)
C(25)	2564(2)	3925(2)	787(2)	32(1)
C(26)	2196(2)	3458(2)	1825(2)	22(1)
C(31)	4314(2)	2559(2)	5783(2)	17(1)
C(32)	4361(2)	1482(2)	6534(2)	21(1)
C(33)	4276(2)	1608(2)	7576(2)	25(1)
C(34)	4157(2)	2777(2)	7855(2)	27(1)
C(35)	4129(2)	3836(2)	7100(2)	25(1)
C(36)	4200(2)	3735(2)	6053(2)	20(1)
C(61)	2215(2)	-1288(2)	8625(2)	18(1)
C(62)	2410(2)	-782(2)	9491(2)	21(1)
C(63)	3598(2)	-978(2)	9859(2)	23(1)
C(64)	4573(2)	-1656(2)	9356(2)	25(1)
C(65)	4368(2)	-2158(2)	8491(2)	26(1)
C(66)	3191(2)	-1980(2)	8121(2)	23(1)
N(1')	619(2)	2378(2)	7751(1)	24(1)
C(2')	286(2)	2533(2)	8742(2)	28(1)
C(3')	254(2)	3671(2)	9060(2)	35(1)
C(4')	574(2)	4689(2)	8331(2)	33(1)
C(5')	916(2)	4536(2)	7310(2)	30(1)
C(6')	922(2)	3375(2)	7051(2)	27(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Diaminopyridine Derivatives.

Substitution of the second chlorine atom in dichloropyridine **2** by an amino group requires high temperature and

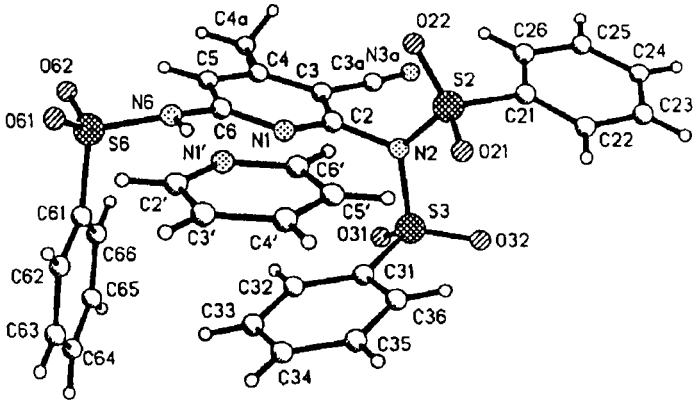


Figure 1. Perspective view and atom labeling of the X-ray structure of **17**.

pressure. A steel reactor charged with dichloropyridine **2** and liquid ammonia to one fourth of its volume (higher loading resulted in explosion) and heated to 150° for 16 hours, gave quantitative conversion to diamine **1** (Scheme 2), which exhibited a singlet at δ 5.74 in the ^{1}H nmr assigned to H-5 and a peak corresponding to C-5 in the ^{13}C nmr at δ 98.8. The significant upfield shift of these resonances (compared to **8**: δ (H-5) 6.34 and δ (C-5) 106.7) reflects the influence of the two electron donating amino groups.

Attempts to alkylate diamine **1** with butyl halides failed. Reaction occurred only at high temperatures (180-200°) and gave complex, inseparable mixtures. Attempted conversion of diamine **1** to a disulfonamido derivative with sodium hydride in dimethyl sulfoxide followed by addition of benzenesulfonyl chloride gave an insoluble tar. However, using pyridine, as both solvent and base, in the benzenesulfonylation of **1** resulted in **14** and **16** in approximately equimolar amounts, but no bisbenzenesulfonylated product. The occurrence of only mono- (**14**) and tris-benzenesulfonylated (**16**) products can be rationalized in kinetics terms indicating a rapid first step, a slow second, and again a rapid third step of the reaction sequence, rather than the expected rapid first and second step, and a slow third step. The molecular structure of **14** was proved by NOE difference spectroscopy; thus, irradiation of the sulfonamido N-H proton (δ 11.15) gave 15% enhancement of the H-5 resonance at δ 6.20. Recrystallization of compound **16** from pyridine gave a stable pyridine adduct **17**. Since several trisbenzenesulfonated isomers are possible and nmr methods are not unequivocal, the structure of **17** was established by X-ray crystallography.

Figure 1 shows a perspective view and atom labeling of the crystal structure. Tables 3 and 4 list atom coordinates and bonding geometries. In the solid state this compound exists as a pyridine solvate with a strong linear hydrogen bond from the sulfonamide NH to the nitrogen of the pyridine solvate. This bond is characterized by the following parameters: N6 ··· N1' 2.745(2) Å, H6 ··· N1' 1.90(2) Å, N6 - H6 ··· N1' 178(1)°. The five aromatic rings are all

Table 4

Bond Lengths (Å) and Angles (°)

S(2)-O(22)	1.421(2)	S(2)-O(21)	1.423(2)
S(2)-N(2)	1.706(2)	S(2)-C(21)	1.760(2)
S(3)-O(31)	1.421(2)	S(3)-O(32)	1.425(2)
S(3)-N(2)	1.688(2)	S(3)-C(31)	1.758(2)
S(6)-O(61)	1.426(2)	S(6)-O(62)	1.428(2)
S(6)-N(6)	1.627(2)	S(5)-C(61)	1.761(2)
N(2)-C(2)	1.451(2)	N(6)-C(6)	1.393(3)
N(1)-C(2)	1.322(3)	N(1)-C(6)	1.339(3)
C(2)-C(3)	1.386(3)	C(3)-C(4)	1.404(3)
C(3)-C(3A)	1.431(3)	C(3A)-N(3A)	1.144(3)
C(4)-C(5)	1.381(3)	C(4)-C(4A)	1.500(3)
C(5)-C(6)	1.395(3)	C(21)-C(22)	1.378(3)
C(21)-C(26)	1.383(3)	C(22)-C(23)	1.385(4)
C(23)-C(24)	1.373(4)	C(24)-C(25)	1.373(4)
C(25)-C(26)	1.385(3)	C(31)-C(36)	1.385(3)
C(31)-C(32)	1.394(3)	C(32)-C(33)	1.380(3)
C(33)-C(34)	1.381(3)	C(34)-C(35)	1.383(3)
C(35)-C(36)	1.380(3)	C(61)-C(62)	1.387(3)
C(61)-C(66)	1.391(3)	C(62)-C(63)	1.383(3)
C(63)-C(64)	1.382(3)	C(64)-C(65)	1.386(3)
C(65)-C(66)	1.374(3)	N(1')-C(2')	1.333(3)
N(1')-C(6')	1.335(3)	C(2')-C(3')	1.377(3)
C(3')-C(4')	1.375(4)	C(4')-C(5')	1.372(4)
C(5')-C(6')	1.372(3)		

O(22)-S(2)-O(21)	120.5(1)	O(22)-S(2)-N(2)	103.1(1)
O(21)-S(2)-N(2)	109.6(1)	O(22)-S(2)-C(21)	109.8(1)
O(21)-S(2)-C(21)	109.0(1)	N(2)-S(2)-C(21)	103.5(1)
O(31)-S(3)-O(32)	120.6(1)	O(31)-S(3)-N(2)	104.9(1)
O(32)-S(3)-N(2)	105.1(1)	O(31)-S(3)-C(31)	108.8(1)
O(32)-S(3)-C(31)	109.6(1)	N(2)-S(3)-C(31)	107.0(1)
O(61)-S(6)-O(62)	119.9(1)	O(61)-S(6)-N(6)	104.9(1)
O(62)-S(6)-N(6)	109.3(1)	O(61)-S(6)-C(61)	107.7(1)
O(62)-S(6)-C(61)	107.5(1)	N(6)-S(6)-C(61)	106.7(1)
C(2)-N(2)-S(3)	116.8(1)	C(2)-N(2)-S(2)	117.2(1)
S(3)-N(2)-S(2)	120.2(1)	C(6)-N(6)-S(6)	127.4(2)
C(2)-N(1)-C(6)	117.3(2)	N(1)-C(2)-C(3)	124.5(2)
N(1)-C(2)-N(2)	115.9(2)	C(3)-C(2)-N(2)	119.6(2)
C(2)-C(3)-C(4)	118.2(2)	C(2)-C(3)-C(3A)	121.6(2)
C(4)-C(3)-C(3A)	120.1(2)	N(3A)-C(3A)-C(3)	176.7(2)
C(5)-C(4)-C(3)	117.7(2)	C(5)-C(4)-C(4A)	121.1(2)
C(3)-C(4)-C(4A)	121.1(2)	C(4)-C(5)-C(6)	119.4(2)
N(1)-C(6)-N(6)	113.1(2)	N(1)-C(6)-C(5)	122.9(2)
N(6)-C(6)-C(5)	123.9(2)	C(22)-C(21)-C(26)	122.0(2)
C(22)-C(21)-S(2)	118.9(2)	C(26)-C(21)-S(2)	119.0(2)
C(21)-C(22)-C(23)	118.3(2)	C(24)-C(23)-C(22)	120.4(2)
C(23)-C(24)-C(25)	120.6(2)	C(24)-C(25)-C(26)	120.1(2)
C(21)-C(26)-C(25)	118.5(2)	C(36)-C(31)-C(32)	122.0(2)
C(36)-C(31)-S(3)	119.6(2)	C(32)-C(31)-S(3)	118.4(2)
C(33)-C(32)-C(31)	118.3(2)	C(32)-C(33)-C(34)	120.2(2)
C(33)-C(34)-C(35)	120.9(2)	C(36)-C(35)-C(34)	120.0(2)
C(35)-C(36)-C(31)	118.6(2)	C(62)-C(61)-C(66)	121.2(2)
C(62)-C(61)-S(6)	119.6(2)	C(66)-C(61)-S(6)	119.2(2)
C(63)-C(62)-C(61)	119.0(2)	C(64)-C(63)-C(62)	120.0(2)
C(63)-C(64)-C(65)	120.6(2)	C(66)-C(65)-C(64)	120.2(2)
C(65)-C(66)-C(61)	119.1(2)	C(2')-N(1')-C(6')	117.8(2)
N(1')-C(2')-C(3')	122.5(2)	C(4')-C(3')-C(2')	119.0(2)
C(5')-C(4')-C(3')	118.8(2)	C(6')-C(5')-C(4')	118.9(2)
N(1')-C(6')-C(5')	122.9(2)		

planar to within 0.007Å with the three phenyl rings inclined to the plane of the pyridine ring at angles of 15.7, 26.6 and 97.9°. The bonding geometry shows no unusual features and there are no unusually short intermolecular contacts.

The sole formation of **16** is attributed to the influence of base. Benzenesulfonylation of the second amino group in **14** gives intermediate **15** which, in the presence of pyridine, immediately produces an anion. Ionization occurs at the 2-benzenesulfonamido group rendered more acidic by electron withdrawing effect of the 3-cyano group. This anion of **15** is evidently more nucleophilic than the amino group in **14**.

We expected that treatment of diamino-pyridine **1** with two molar equivalents of benzenesulfonyl chloride in the absence of base would give derivative **15**, because suppression of its ionization would prevent formation of **16**. However, electrophilic attack on C-5 was observed giving sulfon **12**, together with salt **13**.

EXPERIMENTAL

Melting points, given in degrees Celsius, were determined with a Thomas-Hoover capillary apparatus (up to 200°) and a hot-stage microscope (above 200°) and are uncorrected. Elemental analyses were performed by Mel Courtney of the Chemistry Department, University of Florida. The nmr spectra were obtained on a Varian VXR-300 instrument. All reagents employed were purchased commercially and used without further purification.

2,6-Dihydroxy-4-methyl-3-pyridinecarbonitrile (**6**). Method A.

A mixture of cyanoacetamide (27.62 g, 328 mmoles), ethyl acetoacetate (41.9 ml, 328 mmoles), potassium hydroxide (19.6 g, 350 mmoles) and methanol (400 ml) was stirred and heated at reflux for 6 hours. The reaction mixture was poured into water (500 ml) and then heated to 70° to get a clear solution. After acidification of the solution with 37% hydrochloric acid (50 ml), precipitation started. The mixture was set aside at 20° for 16 hours. The precipitate was collected by filtration, washed with water (50 ml) and dried in a vacuum oven at 60° to give pure **6**, 34.85 g (65% yield) as tiny colorless needles, mp 312-320°, lit [9] 315-320°.

2,6-Dihydroxy-4-methyl-3-pyridinecarbonitrile (**6**). Method B.

To a solution of sodium ethoxide in ethanol, obtained by the reaction of metallic sodium (0.55 g, 24 mmoles) with absolute ethanol (20 ml) were added portionwise ethyl cyanoacetate (2.55 ml, 24 mmoles) and acetoacetamide (2.43 ml, 24 mmoles). The resulting mixture was stirred and heated at reflux for 12 hours. After cooling, the reaction mixture was poured into water (100 ml), acidified with 37% hydrochloric acid to *p*H 1.0 and set aside at 22° for 3 hours. The precipitate obtained was collected by filtration, washed with water (10 ml) and dried in a vacuum oven at 50° to give a white powder, mp 310-318° with nmr spectra identical to those obtained for pure **6**, 1.83 g (46% yield).

2,6-Dichloro-4-methyl-3-pyridinecarbonitrile (**2**).

Compound **6** (3.9 g, 24 mmoles) and phosphorus oxychloride (11.96 g, 78 mmoles) were heated in a steel autoclave at 200° for 7 hours. After cooling to 20°, the pressure was released, the autoclave was opened and its contents were poured into water (50 ml). The suspension obtained was stirred at 22° for 1 hour. The precipitate was filtered off, washed with water (20 ml) and dried in a vacuum oven at 22° to give pure **2** (4.42 g, 98%), mp 109°, lit [9] 109-110°.

6-Amino-2-chloro-4-methyl-3-pyridinecarbonitrile (**8**) and 2-Amino-6-chloro-4-methyl-3-pyridinecarbonitrile (**9**).

A mixture of **2** (7.0 g, 37 mmoles) and liquid ammonia (12.5 g, 623 mmoles) was kept in a teflon coated pressure reactor at 20° for 20 hours. After the pressure was released, the reaction mixture was triturated with water (50 ml). The precipitate was collected by filtration and dried in a vacuum oven at 50° to give a mixture of **8** and **9** in a molar ratio of 73:27, according to nmr. A sample of this mixture (60 mg) was dissolved in chloroform (10 ml) and subjected to column chromatography (wide column packed with 50 g of silica gel) using chloroform as the eluent. Evaporation of the first fraction and recrystallization of the residue from ethanol (5 ml) gave pure **9** (15 mg) as orange prisms, mp 235°.

Anal. Calcd. for $C_7H_6N_3Cl$: C, 50.17; H, 3.61; N, 25.07. Found: C, 50.24; H, 3.62; N, 24.92.

Evaporation of the second fraction and recrystallization of the residue from ethanol (5 ml) gave pure **8** (28 mg) as yellow needles, mp 247°.

Anal. Calcd. for $C_7H_6N_3Cl$: C, 50.17; H, 3.61; N, 25.07. Found: C, 50.48; H, 3.63; N, 25.12.

N-[2-Chloro-3-cyano-4-methylpyridin-6-yl]benzenesulfonamide (**10**) and *N*-[6-Chloro-3-cyano-4-methylpyridin-2-yl]benzenesulfonamide (**11**).

Sodium hydride (0.19 g, 8 mmoles) was added to a solution of aminochloropyridines **8** and **9** (1.0 g, 6.0 mmoles) in dry dimethyl sulfoxide (5 ml) stirred under nitrogen at 20°, the flask was cooled in ice/water and benzenesulfonyl chloride (1.0 ml, 8 mmoles) was added dropwise in a rate not allowing the reaction temperature to exceed 20°. After the addition, the reaction mixture was stirred at 20° for 16 hours, then poured onto crushed ice (30 g) and neutralized with 5% ammonia. The precipitate obtained was collected by filtration, washed with water (10 ml) and recrystallized repeatedly from 70% ethanol to give pure **10** (0.63 g, 34%), yellowish needles, mp 184°.

Anal. Calcd. for $C_{13}H_{10}ClN_3O_2S$: C, 50.73; H, 3.28; N, 13.65. Found: C, 50.58; H, 3.23; N, 13.59.

Combined filtrates from the above recrystallization were collected, evaporated and the residue was twice recrystallized from methanol to give pure sulfonamide **11** (0.12 g, 6%), plates, mp 195°.

Anal. Calcd. for $C_{13}H_{10}ClN_3O_2S$: C, 50.73; H, 3.28; N, 13.65. Found: C, 50.56; H, 3.19; N, 13.57.

2,6-Diamino-4-methyl-3-pyridinecarbonitrile (**1**).

A mixture of 2,6-dichloro-4-methyl-3-pyridinecarbonitrile (**2**) (2.0 g, 10.7 mmoles) and liquid ammonia (5 ml) was heated in a steel bomb at 150° for 16 hours. After cooling to 20°, the pressure was released to allow the excess ammonia to evaporate. The residue was transferred into water (50 ml), neutralized with

acetic acid and the resulting suspension was stirred at 20° for 1 hour. The precipitate was filtered off, washed with water (20 ml) and dried in a vacuum oven at 40° to give pure **1** (1.4 g, 91%) as yellowish prisms, mp 223°, lit [6] mp 225°.

2,6-Diamino-4-methyl-5-benzenesulfonyl-3-pyridinecarbonitrile (**12**).

A mixture of diamine **1** (0.5 g, 3.4 mmoles) and benzenesulfonyl chloride (1.0 ml, 7.8 mmoles) was stirred under nitrogen at 80° for 20 hours. After cooling to 20°, the reaction mixture was triturated with 10% sodium hydroxide (10 ml) and then neutralized with 10% hydrochloric acid. The precipitate was collected by filtration and recrystallized from ethanol to give **12** (0.15 g, 15%) as dark prisms, mp 205°.

Anal. Calcd. for $C_{13}H_{12}N_4O_2S$: C, 54.15; H, 4.20; N, 19.43. Found: C, 54.08; H, 4.16; N, 19.88.

Upon standing at room temperature for 24 hours, the filtrate from **12** deposited crystals of benzenesulfonate **13**, mp 220°.

Anal. Calcd. for $C_{13}H_{14}N_4O_3S$: C, 50.96; H, 4.60; N, 18.29. Found: C, 50.89; H, 4.56; N, 18.45.

2-Benzenesulfonamido-6-bis(benzenesulfon)amido-4-methylpyridinecarbonitrile, Pyridine Adduct (**17**).

Benzenesulfonyl chloride (3.1 ml, 24.3 mmoles) was added to a stirred solution of diamine **1** (1.2 g, 8.1 mmoles) in pyridine (10 ml). The stirring was continued at 20° for 20 hours. The reaction mixture was poured onto crushed ice (100 g) and acetic acid (10 ml). The obtained precipitate was filtered off, and then recrystallized from ethanol to give **16**. Crystallization of **16** from pyridine gave salt **17** (0.95 g, 18%) as colorless prisms, mp 190-198° dec.

Anal. Calcd. for $C_{30}H_{25}N_5O_6S_3$: C, 55.62; H, 3.89; N, 10.81. Found: C, 55.50; H, 3.84; N, 10.83.

Concentration of the mother liquor, after separation of **16**, gave sulfonamide **14** (0.40 g, 17%) as yellowish prisms, mp 228-230°.

Anal. Calcd. for $C_{13}H_{12}N_4O_2S$: C, 54.15; H, 4.20. Found: C, 54.19; H, 4.49.

X-Ray Crystallography.

Intensity data were collected with a Nicolet P4s four-circle diffractometer by using monochromatized MoKα (λ = 0.71073Å) radiation. The crystal used was a colorless block of dimensions 0.69 x 0.35 x 0.27 mm. Throughout data collections the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods using SHELXS90 [12], and refined on F by full-matrix least-squares procedures using SHELXL93 [13]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. CH hydrogen atoms were included in calculated positions with isotropic displacement coefficients equal to 1.3 times the isotropic equivalent of their carrier carbons. The NH hydrogen was located from a difference map and its position refined. The function minimized was $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.0425P^2 + 0.718P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. A final difference map showed no features greater or less than $0.35e^-/Å^3$. Final non-hydrogen atom coordinates, bond lengths and bond angles are listed in Tables 3 and 4. Tabulations of hydrogen atom coordinates, anisotropic thermal parameters, structure factors and equations of meanplanes are available as supplementary material from the author PJS.

Crystal data -140°: $C_{30}H_{25}N_5O_6S_3$, MW = 647.7, triclinic, space group P-1, a = 10.609(2), b = 10.959(2), c = 13.027(3) Å, α = 79.83(3), β = 83.33(3)°, γ = 84.14(3), U = 1475.5(5) $Å^3$, F(000) = 672, Z = 2, D_c = 1.458 g cm^{-3}, $\mu(M_o\text{-}K\alpha)$ = 3.05 cm^{-1}, ω scans, $2\theta_{max}$ = 50°, 275 parameters, S = 1.17, wR2 = 0.087 for all 5183 data, R1 = 0.034 for 4228 data with $F_o > 4\sigma(F_o)$.

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