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SYNTHESIS OF N-PYRIDYLMETHYLIDENE-2-AMINOPYRIDINES AND THEIR METHYL-SUBSTITUTED DERIVATIVES IN THE PRESENCE OF MOLECULAR SIEVES

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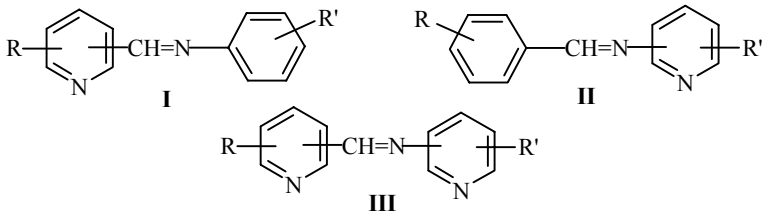
We have studied condensation of 2-, 3-, 4-pyridinealdehydes and 6-methylpyridine-2-aldehyde with 2-aminopyridine and its 3-, 4-, and 6-methyl derivatives in benzene in the presence of molecular sieves. The reactions occur even at room temperature to form the corresponding pyridyl-pyridyl azomethines, and also aminals. We have determined the optimal conditions for carrying out the processes with the aim of obtaining both types of products. We consider the characteristics of the mass spectra for the synthesized aldimines. We present the X-ray diffraction results for the two aminals.

Keywords: aminals, heterocyclic Schiff's bases, 2-pyridylazomethines, pyridylmethylidenes, triazastilbenes, molecular sieves.

A significant number of diazastilbenes **I** and **II** are known: Schiff's bases synthesized by condensations of pyridinealdehydes with aromatic amines or aminopyridines with aromatic aldehydes.



Interest in such compounds is related to their use for synthesis of biologically active substances [1, 2], use as selective adsorbents of metal ions [3], and their ability to form mesophases [4]. Their structure and physical properties [5-10] and also complexes of their homologs with various metals [11-13] have been studied. Triazastilbenes **III** have been considerably less studied (as far as we know, only N-4-pyridylmethylidene-4-aminopyridine has been synthesized by condensation of the corresponding aldehyde and amine upon boiling in xylene for 16 h with distillation of the azeotrope [14]), while the 2-aminopyridine derivatives have not been described. An attempt [15] to obtain a compound of structure **III** by condensation of 2-pyridinealdehyde with 2-aminopyridine proved to be unsuccessful, since the only isolated product was the corresponding aminal, while data in [16] on synthesis of this aldimine and its methyl-substituted derivatives are probably erroneous, which has already been pointed out by the authors of [15]. Homologs of triazastilbenes have been studied as tridentate chelating ligands [17, 18].

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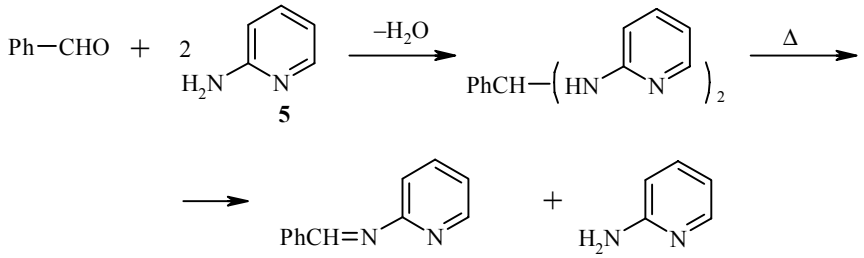
SYNTHESIS OF ALDIMINES AND AMINALS

We previously [19-22] successfully used molecular sieves (MS) to carry out dehydrocondensations, including with participation of 2-aminopyridines. Using this experience, in this research we studied the reaction of pyridinealdehydes **1-4** with a series of 2-aminopyridines **5-8**, with the aim of synthesizing the corresponding products (see Scheme 1), azomethines **1a-16a**: potential polyfunctional synthons, prochiral substrates, and also precursors of biologically active compounds.

As follows from the data in [15, 23-25] and our papers [19, 21], the major problem in synthesis of imines based on 2-aminopyridines is formation of aminals. In [23], it was established that in the reaction of benzaldehyde with amine **5**, the primary product is the aminal, which is converted to the aldimine upon subsequent thermal decomposition.

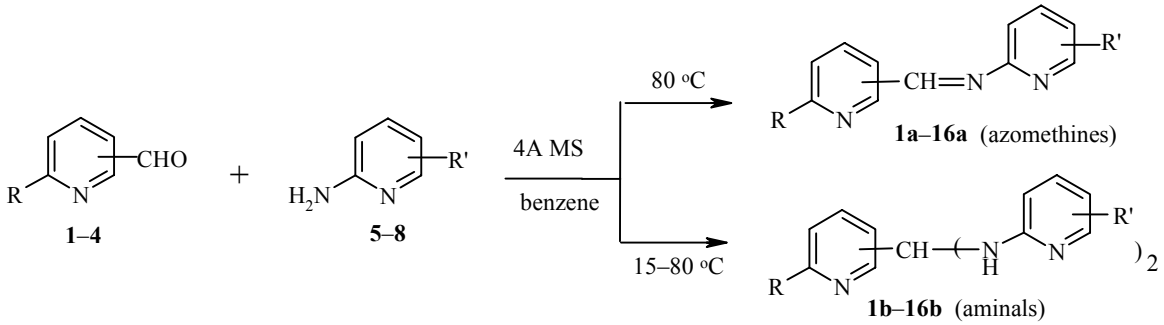


In the case of synthesis of 2-pyridylazopyridylmethines, the problem is aggravated by the instability of these compounds. Our research showed that in the presence of molecular sieves, condensations of almost all the substrates occur even at room temperature. Evidence for this comes from data from analysis of the reaction mixtures by TLC and chromatomass spectrometry (GLC-MS), recording the decrease in concentration (and in some cases, also complete conversion) of the starting compounds and the appearance of aldimines. Aminals, due to their thermal instability and instability in many solvents, are not detected by TLC, GLC-MS, or liquid chromatography. We inferred their appearance in significant amounts in the reaction mixture from the precipitates falling out of benzene (all the aldimines and substrates are quite soluble in benzene). Thus even at 20°C, both types of products are formed, despite the fact that the starting compounds were used in equimolar amounts. Isolation of aldimines from the mixtures proved to be impossible in most cases: they almost completely decompose upon vacuum distillation, sublimation, or column chromatography. We were able to isolate both types of products (**13a, 13b** and **15a, 15b**) from their mixtures by fractional crystallization only for condensations of 6-methylpyridine-2-aldehyde with amines **5** and **7** (runs 28, 32, Table 1). Hypothesizing that elevated temperature would promote decomposition of aminals and thus an increase in the yield of aldimines, with the aim of obtaining the latter we carried out the reactions with boiling in benzene (we also carried out runs using toluene and xylene as the higher boiling solvents, but this did not improve the results due to tar formation for both the substrates and the products). We synthesized almost all the aldimines (**1a-14a, 16a**) in this way. In some cases, they were sufficiently pure (**5a-12a, 14a**) and were obtained in high yields (82% to 98%). The remaining aldimines were recrystallized from hexane or benzene in 57 to 68% yield. The mass spectra and the ^{1}H NMR spectra of all the synthesized aldimines are presented in Tables 2 and 3 and correspond to their structures.

The aminals were synthesized by several methods. Compounds **5b-7b, 14b, 16b** were obtained in 49 to 58% yields when the reactions were carried out at room temperature (starting aldehyde–amine mole ratio, 1:2) for 20 h. The precipitates formed were separated from the sieves, some were additionally purified with ether or benzene, after which all the characteristics corresponded to the structure. Aminals **1b-4b , 8b** were formed more slowly. After condensation at 20°C for 20 h, precipitates did not fall out but there was considerable conversion of the substrate (GLC-MS). Considering this fact, the sieve was filtered out and the filtrate was held at room

Scheme 1

Condensation of Pyridinealdehydes with 2-Aminopyridines in the Presence of Molecular Sieves (MS)



Aldehyde	R	CHO position	Amine	R
1	H	2-	**5**	H
2	H	3-	**6**	3-CH_3
3	H	4-	**7**	4-CH_3
4	CH_3	2-	**8**	6-CH_3

Starting aldehyde	Starting amine	Products	Starting aldehyde	Starting amine	Products
1	**5**	**1a,b**	**3**	**5**	**9a,b**
1	**6**	**2a,b**	**3**	**6**	**10a,b**
1	**7**	**3a,b**	**3**	**7**	**11a,b**
1	**8**	**4a,b**	**3**	**8**	**12a,b**
2	**5**	**5a,b**	**4**	**5**	**13a,b**
2	**6**	**6a,b**	**4**	**6**	**14a,b**
2	**7**	**7a,b**	**4**	**7**	**15a,b**
2	**8**	**8a,b**	**4**	**8**	**16a,b**

TABLE 1. Characteristics of Condensation Products

Run	Starting aldehyde–amine ratio, moles	Reaction temperature, °C (time, h)	Product	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %*
					C	H	N		
1	2	3	4	5	6	7	8	9	10
1	1:1	80 (5)	**1a**	$C_{11}H_9N_3$	71.86 72.11	4.93 4.95	23.00 22.93	67-68	60 (hexane)
2	1:1	80 (5)	**1b**	$C_{16}H_{15}N_5$	68.85 69.30	5.37 5.45	24.98 25.25	118-120 (117-119 [15])	95 (AcOEt–hexane)
3	1:2	20 (20); 20 (48)*[2]	**1b**	$C_{16}H_{15}N_5$	69.07 69.30	5.36 5.45	25.07 25.25	116-117	59 (ether)
4	1:1	80 (5)	**2a**	$C_{12}H_{11}N_3$	72.98 73.08	5.65 5.62	21.29 21.30	33-34	68 (hexane)
5	1:1	80 (5)	**2b**	$C_{18}H_{19}N_5$	70.87 70.80	6.23 6.27	22.83 22.93	123-124	98 (AcOEt–hexane)
6	1:2	20 (20); 20 (48)*[2]	**2b**	$C_{18}H_{19}N_5$	70.86 70.80	6.22 6.27	22.81 22.93	120-122	56 (ether)
7	1:1	80 (5)	**3a**	$C_{12}H_{11}N_3$	72.74 73.08	5.54 5.62	20.72 21.30	47-48	65 (hexane)
8	1:1	80 (5)	**3b**	$C_{18}H_{19}N_5$	70.54 70.80	6.18 6.27	22.71 22.93	105-107	84 (AcOEt–hexane)
9	1:2	20 (20); 20 (48)*[2]	**3b**	$C_{18}H_{19}N_5$	70.74 70.80	6.24 6.27	22.65 22.93	104-106	57 (ether)
10	1:1	80 (5)	**4a**	$C_{12}H_{11}N_3$	72.84 73.08	5.62 5.62	21.21 21.30	40-45	63 (hexane)

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
11	1:2	20 (20); 20 (48)*[2]	**4b**	$C_{18}H_{19}N_5$	70.84 70.80	6.26 6.27	22.97 22.93	85-86	67 (ether)
12	1:1	80 (5)	**5a**	$C_{11}H_9N_3$	71.81 72.11	4.69 4.95	22.60 22.93	60	82
13	1:2	20 (20)	**5b**	$C_{16}H_{15}N_5$	69.35 69.30	5.45 5.45	25.08 25.25	136-137	58
14	1:1	80 (5)	**6a**	$C_{12}H_{11}N_3$	72.91 73.08	5.68 5.62	21.18 21.30	20-23	91
15	1:2	20 (20)	**6b**	$C_{18}H_{19}N_5$	70.76 70.80	6.27 6.27	23.01 22.93	113-115	54 (ether)
16	1:1	80 (5)	**7a**	$C_{12}H_{11}N_3$	72.98 73.08	5.73 5.62	21.40 21.30	66-67	91
17	1:2	20 (20)	**7b**	$C_{18}H_{19}N_5$	70.82 70.80	6.29 6.27	22.73 22.93	117-118	49
18	1:1	80 (5)	**8a**	$C_{12}H_{11}N_3$	73.19 73.08	5.86 5.62	21.14 21.30	45-46	98
19	1:2	20 (70); 20 (48)*[2]; 80 (5)	**8b**	$C_{18}H_{19}N_5$	70.44 70.80	6.22 6.27	22.66 22.93	88-89	45 (ether–hexane)
20	1:1	80 (5)	**9a**	$C_{11}H_9N_3$	72.02 72.11	5.08 4.95	22.88 22.93	35-36	98
21	1:2	15 (40); 20 (60)*[2]	**9b**	$C_{16}H_{15}N_5$	69.19 69.30	5.51 5.45	25.24 25.25	144-146	75 (ether)
22	1:1	80 (5)	**10a**	$C_{12}H_{11}N_3$	72.86 73.08	5.62 5.62	21.20 21.30	39-40	95
23	1:2	15 (40); 20 (60)*[2]	**10b**	$C_{18}H_{19}N_5$	70.67 70.80	6.29 6.27	22.88 22.93	123-125	67 (ether–hexane)
24	1:1	80 (5)	**11a**	$C_{12}H_{11}N_3$	72.88 73.08	5.74 5.62	21.32 21.30	36-38	96

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
25	1:2	15 (40)	**11b**	$C_{18}H_{19}N_5$	70.52 70.80	6.16 6.27	22.95 22.93	130-132	60 (ether)
26	1:1	80 (5)	**12a**	$C_{12}H_{11}N_3$	72.99 73.08	5.85 5.62	21.43 21.30	33-35	97
27	1:2	15 (40)	**12b**	$C_{18}H_{19}N_5$	70.64 70.80	6.30 6.27	22.87 22.93	116-118	59 (ether)
28	1:1	20 (20)	**13a**	$C_{12}H_{11}N_3$	72.95 73.08	5.51 5.62	21.20 21.30	68-70	60 (benzene)
			13b	$C_{17}H_{17}N_5$	70.18 70.08	5.83 5.88	23.98 24.04	122-124	30
29	1:1	80 (5)	**13a**	$C_{12}H_{11}N_3$	73.00 73.08	5.55 5.62	21.45 21.30	55-60	61 (benzene)
30	1:1	80 (5)	**14a**	$C_{13}H_{13}N_3$	73.95 73.91	6.12 6.20	19.69 19.89	31-34	98
31	1:2	20 (20)	**14b**	$C_{19}H_{21}N_5$	71.38 71.45	6.61 6.63	21.73 21.93	113-116	55 (benzene)
32	1:1	20 (20)	**15a**	$C_{13}H_{13}N_3$	73.43 73.91	6.25 6.20	19.96 19.89	96-97	25
	1:1	20 (20)	**15b**	$C_{19}H_{21}N_5$	71.60 71.45	6.64 6.63	21.77 21.93	106-107	45
33	1:1	80 (5)	**16a**	$C_{13}H_{13}N_3$	73.88 73.91	6.20 6.20	19.73 19.89	33-36	57 (benzene)
34	1:2	20 (20)	**16b**	$C_{19}H_{21}N_5$	71.58 71.45	6.64 6.63	21.67 21.93	134-135	55 (benzene)

* The recrystallization solvent is indicated in parentheses.

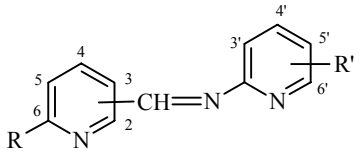
*[2] Without molecular sieve.

TABLE 2. Mass Spectra* of Aldimines (ArCH=NAr') **1a-16a**

Com-pound	*m*/*z* (I_{rel}, %)											
	M^+	$[M–H]^+$	$[M–Me]^+$	$[M–HCN]^+$	$[M–HCN–H]^+$	$[M–Me–HCN]^+$	$[M–Ar]^+$	$[M–Ar']^+$	$Ar'H^+$	ArH^+	Ar'^{+}	Ar^+
1a	183 (45)	182 (**100**)	—	156 (44)	155 (36)	—	105 (22)		79 (57)		78 (59)	
2a	197 (34)	196 (76)	182 (**100**)	170 (13)	169 (82)	155 (2)	119 (43)	105 (15)	93 (54)	79 (11)	92 (32)	78 (20)
3a	197 (41)	196 (**100**)	182 (11)	170 (36)	169 (45)	155 (5)	119 (5)	105 (11)	93 (73)	79 (8)	92 (27)	78 (16)
4a	197 (27)	196 (46)	182 (3)	170 (9)	169 (45)	155 (5)	119 (6)	105 (11)	93 (**100**)	79 (8)	92 (21)	78 (15)
5a	183 (15)	182 (**100**)	—	156 (9)	155 (15)	—	105 (22)		79 (33)		78 (20)	
6a	197 (19)	196 (**100**)	182 (12)	170 (4)	169 (22)	155 (2)	119 (4)	105 (3)	93 (35)	—	92 (14)	78 (5)
7a	197 (16)	196 (**100**)	182 (4)	170 (6)	169 (14)	155 (2)	119 (1)	105 (2)	93 (31)	—	92 (6)	78 (5)
8a	197 (20)	196 (48)	182 (1)	170 (14)	169 (13)	155 (4)	119 (1)	105 (4)	93 (**100**)	—	92 (13)	78 (6)
9a	183 (37)	182 (**100**)	—	156 (10)	155 (20)	—	105 (22)		79 (90)		78 (39)	
10a	197 (46)	196 (**100**)	182 (15)	170 (7)	169 (36)	155 (3)	119 (14)	105 (6)	93 (86)	—	92 (27)	78 (8)
11a	197 (32)	196 (**100**)	182 (4)	170 (9)	169 (19)	155 (3)	119 (2)	105 (3)	93 (60)	—	92 (14)	78 (6)
12a	197 (16)	196 (23)	182 (1)	170 (7)	169 (13)	155 (2)	119 (2)	105 (3)	93 (**100**)	—	92 (13)	78 (6)
13a	197 (28)	196 (**100**)	182 (1)	170 (12)	169 (54)	155 (5)	—	119 (40)	79 (41)	93 (11)	78 (36)	92 (10)
14a	211 (33)	210 (**100**)	196 (9)	184 (3)	183 (19)	169 (22)	119 (67)		93 (63)		92 (31)	
15a	211 (28)	210 (**100**)	196 (4)	184 (13)	183 (56)	169 (7)	119 (15)		93 (44)		92 (22)	
16a	211 (24)	210 (13)	196 (2)	184 (10)	183 (40)	169 (6)	119 (28)		93 (**100**)		92 (23)	

* The signals for the characteristic ions are indicated. Peaks with *m*/*z* under 78 are not given.

TABLE 3. ^{1}H NMR Spectra of Aldimines **1a-16a**



Com-pound	Chemical shifts, δ, ppm ($CDCl_3$), spin-spin coupling constants, *J*, Hz		
	CH=, s	CH_3, s	Protons of pyridine rings
1	2	3	4
1a	9.19	—	7.20 (ddd, *J* = 1.2, 4.7, 7.5, H-5'); 7.3-7.4 (2H, m, H-3, H-5); 7.77 (td, *J* = 2.0, 8.0. H-4); 7.81 (td, *J* = 1.8, 7.5, H-4'); 8.20 (dd, *J* = 1.2, 7.5, H-3'); 8.52 (ddd, *J* = 0.8, 2.0, 5.0, H-6); 8.75 (ddd, *J* = 0.8, 1.8, 4.7, H-6')
2a	9.12	2.45	7.10 (dd, *J* = 5.0, 7.6, H-5'); 7.35 (ddd, *J* = 0.6, 4.8, 7.6, H-5); 7.54 (dd, *J* = 0.8, 7.6, H-4'); 7.79 (td, *J* = 0.8, 7.6, H-4); 8.26 (dd, *J* = 0.6, 7.6, H-3); 8.31 (dd, *J* = 0.8, 5.0, H-6'); 8.73 (dd, *J* = 0.8, 4.8, H-6)
3a	9.16	2.39	7.03 (d, *J* = 5.0, H-5'); 7.19 (s, H-3'); 7.36 (ddd, *J* = 1.2, 4.9, 6.2, H-5); 7.81 (td, *J* = 1.6, 7.7, H-4); 8.19 (ddd, *J* = 0.8, 1.2, 7.7, H-3); 8.37 (d, *J* = 5.0, H-6'); 8.75 (ddd, *J* = 0.8, 1.6, 4.9, H-6)
4a	9.14	2.56	7.06 (d, *J* = 7.6, H-5'); 7.13 (d, *J* = 7.6, H-3); 7.36 (dd, *J* = 1.6, 8.0, H-4'); 7.41 (dd, *J* = 5.0, 8.0, H-5); 7.77 (td, *J* = 2.0, 7.6, H-4); 8.35 (dd, *J* = 1.8, 8.0, H-3'); 8.50 (dd, *J* = 2.0, 5.0, H-6)
5a	9.22	—	7.21 (ddd, *J* = 1.7, 4.6, 7.8, H-5'); 7.36 (dd, *J* = 1.7, 7.8, H-3'); 7.41 (dd, *J* = 5.0, 8.0, H-5); 7.77 (td, *J* = 2.0, 7.8, H-4'); 8.35 (dd, *J* = 1.7, 8.0, H-4); 8.50 (dd, *J* = 2.0, 4.6, H-6'); 8.71 (dd, *J* = 1.7, 5.0, H-6); 9.10 (d, *J* = 1.8, H-2)
6a	9.15	2.46	7.11 (dd, *J* = 4.8, 7.6, H-5'); 7.40 (dd, *J* = 4.8, 7.8, H-5); 7.56 (dd, *J* = 1.6, 7.6, H-4'); 8.30 (dd, *J* = 1.6, 4.8, H-6'); 8.37 (dd, *J* = 1.8, 7.8, H-4); 8.70 (dd, *J* = 1.8, 4.8, H-6); 9.12 (d, *J* = 1.8, H-2)

TABLE 3 (continued)

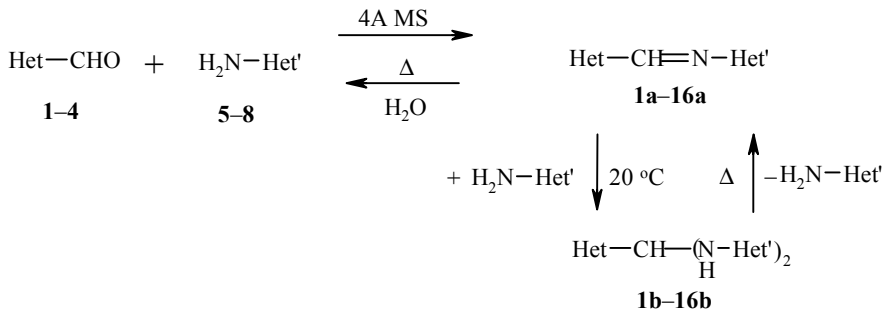
1	2	3	4
7a	9.22	2.40	7.03 (d, *J* = 5.4, H-5'); 7.18 (s, H-3'); 7.41 (dd, *J* = 5.0, 8.0, H-5); 8.33 (dd, *J* = 2.0, 8.0, H-4); 8.35 (d, *J* = 5.4, H-6'); 8.71 (dd, *J* = 2.0, 5.0, H-6); 9.09 (d, *J* = 1.8, H-2)
8a	9.16	2.57	7.07 (d, *J* = 8.0, H-5'); 7.12 (d, *J* = 8.0, H-3'); 7.40 (dd, *J* = 5.0, 8.0, H-5); 7.64 (t, *J* = 8.0, H-4'); 8.35 (dd, *J* = 2.0, 8.0, H-4); 8.70 (dd, *J* = 2.0, 5.0, H-6); 9.09 (d, *J* = 1.4, H-2)
9a	9.17	—	7.22 (ddd, *J* = 1.2, 4.6, 7.2, H-5'); 7.37 (ddd, *J* = 0.8, 1.2, 7.2, H-3'); 7.78 (2H, td, *J* = 2.0, 7.2, H-4'); 7.81 (2H, dd, *J* = 1.4, 4.4, H-3, H-5); 8.51 (ddd, *J* = 0.8, 2.0, 4.6, H-6'); 8.76 (2H, dd, *J* = 1.4, 4.4, H-2, H-6)
10a	9.10	2.47	7.13 (dd, *J* = 5.0, 7.6, H-5'); 7.57 (ddd, *J* = 0.8, 1.4, 7.6, H-4'); 7.82 (dd, *J* = 1.4, 4.4, H-3, H-5); 8.31 (dd, *J* = 1.4, 5.0, H-6'); 8.76 (dd, *J* = 1.4, 4.4, H-2, H-6)
11a	9.16	2.40	7.05 (d, *J* = 5.0, H-5'); 7.21 (d, *J* = 0.8, H-3'); 7.80 (2H, dd, *J* = 1.4, 4.4, H-3, H-5); 8.36 (d, *J* = 5.0, H-6'); 8.76 (2H, dd, *J* = 14, 4.4, H-2, H-6)
12a	9.12	2.57	7.09 (d, *J* = 8.0, H-5'); 7.15 (d, *J* = 8.0, H-3'); 7.66 (t, *J* = 8.0, H-4'); 7.81 (2H, d, *J* = 5.8, H-3, H-5); 8.75 (2H, d, *J* = 5.8, H-2, H-6)
13a	9.14	2.64	7.18 (ddd, *J* = 1.0, 4.6, 7.8, H-5'); 7.23 (d, *J* = 7.8, H-5); 7.35 (d, *J* = 7.8, H-3); 7.70 (t, *J* = 7.8, H-4); 7.76 (td, *J* = 1.9, 7.8, H-4'); 8.00 (d, *J* = 7.8, H-3'); 8.50 (ddd, *J* = 1.0, 1.9, 4.6, H-6')
14a	9.09	2.44; 2.62	7.08 (dd, *J* = 4.4, 8.0, H-5'); 7.22 (d, *J* = 8.0, H-5); 7.53 (d, *J* = 8.0, H-4'); 7.68 (d, *J* = 8.0, H-4); 8.06 (d, *J* = 8.0, H-3); 8.29 (d, *J* = 4.4, H-6')
15a	9.12	2.39; 2.64	7.01 (d, *J* = 5.2, H-5'); 7.17 (s, H-3'); 7.22 (d, *J* = 7.4, H-5); 7.70 (t, *J* = 7.4, H-4); 8.00 (d, *J* = 7.4, H-3); 8.36 (d, *J* = 5.2, H-6')
16a	9.12	2.55; 2.63	7.05 (d, *J* = 7.6, H-5); 7.12 (d, *J* = 7.6, H-3); 7.23 (d, *J* = 8.0, H-5'); 7.63 (t, *J* = 8.0, H-4'); 7.69 (t, *J* = 7.6, H-4); 8.06 (d, *J* = 8.0, H-3')

temperature for another 48 h. After this, the precipitates formed were filtered off and purified with ether, and the aminals **1b-4b** were obtained in 56 to 67% yield. Aminal **8b** was obtained as a result of additional boiling of the mixture for 5 h. After cooling down and holding in a refrigerator, the precipitate formed was purified with ether and hexane (yield 45%). In order to obtain aminals **9b-12b** (and to avoid formation of the corresponding aldimines), condensations of the most reactive 4-pyridinealdehyde were conducted in a cryostat at reduced temperature (15°C). The rest of the reaction conditions and the characteristics of the products are given in Table 1 (runs 21, 23, 25, 27). Aminals **1b-3b** were also synthesized according to the method in [15]. The reactions were conducted as in synthesis of aldimines (for an aldehyde–amine ratio of 1:1). After removal of the sieves and evaporation of the benzene, the residue was recrystallized from a 1:1 ethylacetate–hexane mixture, and the aminals were obtained in high yield (84% to 98% calculated on the basis of the starting amine, runs 2, 5, 8).

The ^{1}H NMR spectra for all the aminals are consistent with their structure (Table 4). Recording the spectra of the aminals presented some difficulty due to their instability in solutions, which has already been noted in [24] in an investigation of other aminals. The mass spectra of the aminals we synthesized completely coincide with the spectra of the corresponding aldimines (the molecular ion signal is missing). The same was observed by the authors of [15], who were studying N,N'-benzylidenebis-2-aminopyridine.

Our studies allow us to draw some conclusions concerning the directions of the interconversions of aldimines and aminals. The aldehydes and amines are condensed at elevated temperature in the presence of a dehydrating agent, forming aldimines. The latter are easily hydrated to the starting aldehyde and amine. Reacting with the amine at room temperature, the aldimines are converted to aminals, which give the reverse reaction with thermal decomposition:

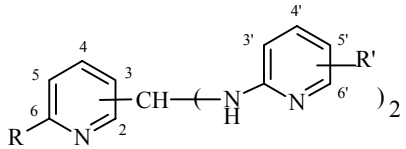
Interconversions of Aldimines 1a-16a and Aminals 1b-16b



MASS SPECTRAL STUDY OF ALDIMINES

In the mass spectra (Table 2) of all the aldimines, the molecular ion signal is not the maximum peak but rather in most cases the $[M–H]^+$ ions have the greatest intensity (exceptions are aldimine **2a**, $[M–Me]^+$ – 100%, and all derivatives of 2-amino-6-methylpyridine, in the spectra of which the $Ar'H^+$ peak is maximum). This distinguishes the spectra of the heterocyclic compounds **1a-16a** from the spectra of benzylideneanilines [15, 26]. For the latter, 100% intensity of the M^+ peak is typical while the intensity of the $[M–1]^+$ ion is significantly lower, which suggests it is formed with difficulty. As shown by studies with deuterated compounds [15], the proton in these aldimines is abstracted from the azomethine group with the charge localized on the nitrogen atom Ph–CH=N^+–Ph. The ease with which the proton is lost in the previously studied [5, 15] *ortho* derivatives, 2-pyridylmethylideneanilines and benzylidene-2-aminopyridines, is connected with the possibility of charge localization on the nitrogen atom of the ring and subsequent formation of favorable cyclic structures. In Scheme 2 (for the example of aldimine **1a**), we show hypothetical fragmentation routes and a possible structure for the

TABLE 4. [1]H NMR Spectra of Aminals **1b-16b**



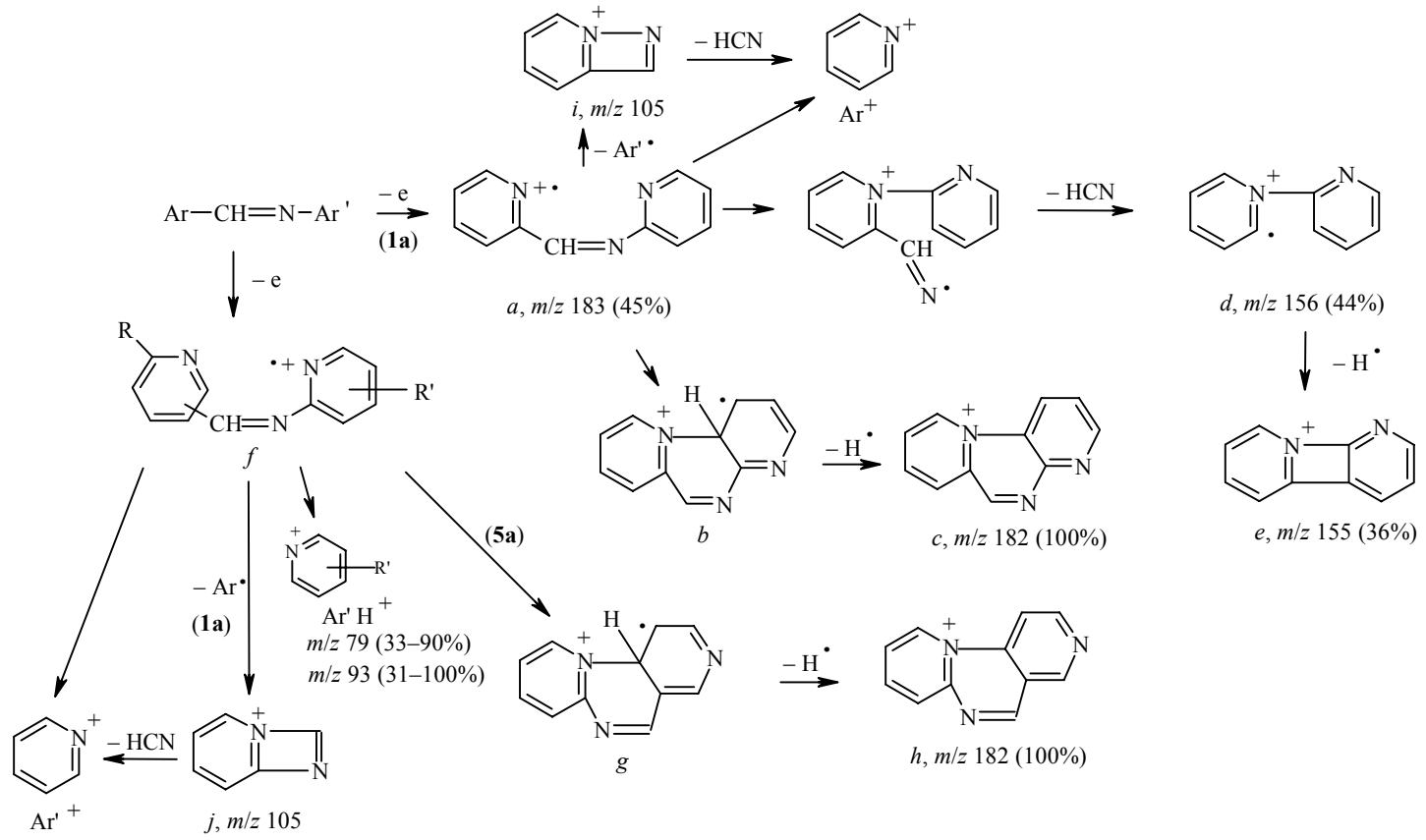
Compound (solvent)	Chemical shifts, δ, ppm, spin-spin coupling constants, *J*, Hz				Stability in solvents ($CDCl_3$, $(CD_3)_2SO$)
	CH, t	NH, d	CH_3, s	Protons of pyridine rings	
1	2	3	4	5	6
1b ($CDCl_3$)	6.84 (1H) *J* = 7.6	5.92 (2H)	—	6.4-6.6 (m, H-3', H-5'); 7.3-7.4 (m, *J* = 6.8, H-3, H-5); 7.5-7.7 (m, *J* = 1.8, 6.8, 7.6, H-4, H-4'); 8.11 (m, *J* = 6.8, H-6'); 8.56 (dd, *J* = 1.4, 5.0, H-6)	Unstable
2b ($CDCl_3$)	7.15 (1H) *J* = 7.0	5.96 (2H)	2.13 (6H)	6.52 (dd, *J* = 5.0, 7.3, H-5'); 7.20 (d, *J* = 7.3, H-4'); 7.27 (dd, *J* = 4.8, 7.3, H-5); 7.63 (td, *J* = 1.6, 7.6, H-4); 7.76 (d, *J* = 7.6, H-3); 7.98 (dd, *J* = 1.6, 5.0, H-6'); 8.58 (d, *J* = 4.8, H-6)	Stable
3b ($CDCl_3$)	6.81 (1H) *J* = 7.6	5.77 (2H)	2.16 (6H)	6.38 (s, H-3'); 6.43 (d, *J* = 4.8, H-5'); 7.19 (dd, *J* = 1.2, 4.5, 7.2, H-5); 7.55 (d, *J* = 7.2, H-3); 7.63 (td, *J* = 0.8, 7.2, H-4); 7.98 (d, *J* = 4.8, H-6'); 8.56 (d, *J* = 4.5, H-6)	Unstable
4b ($CDCl_3$)	6.76 (1H) *J* = 7.2	5.80 (2H)	2.36 (6H)	6.38 (d, *J* = 8.2, H-5'); 6.46 (d, *J* = 8.2, H-3'); 7.17 (d, *J* = 7.6, H-3); 7.25 (d, *J* = 8.2, H-4'); 7.32 (dd, *J* = 1.0, 5.0, 7.6, H-5); 7.64 (td, *J* = 0.8, 7.6, H-4); 8.55 (d, *J* = 5.0, H-6)	Unstable
5b (C_6D_6)	6.24 (1H) *J* = 7.8	4.49 (2H)	—	5.93 (d, *J* = 8.2, H-3'); 6.22 (m, *J* = 5.2, 6.8, H-5'); 6.59 (dd, *J* = 4.8, 7.6, H-5); 6.86 (m, *J* = 6.8, 8.2, H-4'); 7.40 (d, *J* = 7.6, H-4); 7.99 (dd, *J* = 5.2, H-6'); 8.08 (dd, *J* = 4.8, H-6); 8.90 (s, H-2)	Unstable
6b ($(CD_3)_2SO$)	7.41 (1H) *J* = 8.3	6.74 (2H)	2.09 (6H)	6.52 (dd, *J* = 4.8, 6.8, H-5'); 7.29 (d, *J* = 6.8, H-4'); 7.3-7.4 (m, H-5); 7.83 (d, *J* = 6.6, H-4); 7.86 (d, *J* = 4.8, H-6'); 8.39 (d, *J* = 4.4, H-6); 8.65 (d, *J* = 2.0, H-2)	Stable
7b ($(CD_3)_2SO$)	3.33, br. s (3H)		2.13 (6H)	6.3-6.5 (m, H-5', H-5); 7.00 (s, H-3'); 7.38 (dd, *J* = 1.0, 4.4, H-4); 7.82 (d, *J* = 5.2, H-6'); 8.44 (dd, *J* = 2.0, 5.0, H-6); 8.64 (d, *J* = 2.6, H-2)	Unstable (in $CDCl_3$, completely converted to aldimine + amine)

TABLE 4 (continued)

1	2	3	4	5	6
8b ($(CD_3)_2SO$)	6.88 (1H)	7.01 (2H)	2.21 (6H)	6.40 (d, *J* = 7.6, H-3', H-5'); 7.29 (t, *J* = 7.6, H-4'); 7.35 (dd, *J* = 4.8, 7.6, H-5); 7.88 (d, *J* = 7.6, H-4); 8.45 (d, *J* = 4.8, H-6); 8.70 (s, H-2)	Unstable (in $CDCl_3$, completely converted to imine + amine)
	J = 8.0				
9b ($(CD_3)_2SO$)	6.93 (1H)	7.21 (2H)	—	6.53 (dd, *J* = 4.8, 6.2, H-5'); 6.62 (d, *J* = 8.6, H-3'); 7.38 (dd, *J* = 1.4, 6.2, 8.6, H-4'); 7.44 (dd, *J* = 1.4, 4.4, H-3, H-5); 7.95 (dd, *J* = 1.4, 4.8, H-6'); 8.51 (dd, *J* = 1.4, 4.4, H-2, H-6)	Stable in $(CD_3)_2SO$, unstable in $CHCl_3$
	J = 7.6				
10b ($CDCl_3$)	6.96 (1H)	6.13 (2H)	2.12 (6H)	6.54 (dd, *J* = 5.0, 7.2, H-5'); 7.22 (dd, *J* = 1.2, 7.2, H-4'); 7.51 (dd, *J* = 1.4, 4.6, H-3, H-5); 7.89 (dd, *J* = 1.2, 5.0, H-6'); 8.52 (dd, *J* = 1.4, 4.6, H-2, H-6)	Unstable
	J = 8.0				
11b ($(CD_3)_2SO$)	6.91 br. s (1H)	5.72 br. s (2H)	2.12 (6H)	6.39 (d, *J* = 4.9, H-5'); 6.44 (s, H-3'); 7.42 (d, *J* = 4.9, H-6'); 7.81 (d, *J* = 5.3, H-3, H-5); 8.50 (d, *J* = 5.3, H,-2, H-6)	Stable
12b ($(CD_3)_2SO$) + ($CDCl_3$)	6.73 (1H)	5.69 (2H)	2.33 (6H)	6.29 (d, *J* = 7.8, H-5'); 6.47 (d, *J* = 7.8, H-3'); 7.29 (t, *J* = 7.8, H-4'); 7.49 (dd, *J* = 2.0, 4.8, H-3, H-5); 8.53 (dd, *J* = 2.0, 4.8, H-2, H-6)	Unstable
	J = 8.0				
12b ($(CD_3)_2SO$)	6.90 (1H)	6.40 (2H)	2.20 (6H)	6.22 (d, *J* = 7.8, H-5'); 6.31 (d, *J* = 7.8, H-3'); 7.23 (t, *J* = 7.8, H-4'); 7.47 (dd, *J* = 1.4, 4.6, H-3, H-5); 8.51 (dd, *J* = 1.4, 4.6, H-2, H-6)	Unstable
	J = 8.0				
13b ($(CD_3)_2SO$)	6.84 (1H)	7.02 (2H)	3.35 (3H)	6.54 (dd, *J* = 5.2, 7.2, H-5'); 6.59 (d, *J* = 7.2, H-3'); 7.17 (d, *J* = 7.6, H-5); 7.33 (d, *J* = 7.6, H-3); 7.36 (td, *J* = 2.0, 7.2, H-4'); 7.66 (t, *J* = 7.6, H-4); 8.00 (m, *J* = 2.0, 5.2, H-6')	Stable in $(CD_3)_2SO$, unstable in $CDCl_3$
	J = 7.4				
14b ($CDCl_3$)	6.60 (1H)	5.91 (2H)	2.11 (6H) 2.55 (3H)	6.50 (dd, *J* = 5.0, 7.2, H-5'); 7.01 (d, *J* = 6.8, H-5); 7.1-7.2 (m, *J* = 7.2, H-4', H-4); 7.47 (d, *J* = 6.8, H-3); 7.98 (dd, *J* = 1.4, 5.0, H-6')	Stable
	J = 6.8				
15b ($CDCl_3$)	6.78 (1H)	5.78 (2H)	2.17 (6H) 2.55 (3H)	6.40 (s, H-3'); 6.44 (d, *J* = 7.6, H-5'); 7.05 (d, *J* = 7.5, H-5); 7.30 (d, *J* = 7.5, H-3); 7.52 (t, *J* = 7.5, H-4); 7.75 (d, *J* = 7.6, H-6')	Unstable
	J = 7.6				
15b ($(CD_3)_2SO$)	6.84, br. s (1H)	5.72, br. s (2H)	2.11 (6H) 2.49 (3H)	6.39 (s, H-5'); 6.41 (s, *J* = 7.6, H-3'); 7.16 (d, *J* = 7.8, H-5); 7.30 (d, *J* = 7.8, H-3); 7.36 (t, *J* = 7.8, H-4); 7.85 (d, *J* = 4.6, H-6')	Unstable
16b ($CDCl_3$)	6.72 (1H)	5.76 (2H)	2.37 (6H) 2.55 (3H)	6.39 (d, *J* = 7.8, H-5'); 6.46 (d, *J* = 7.8, H-3'); 7.25 (d, *J* = 7.5, H-5); 7.25 (t, *J* = 7.8, H-4'); 7.33 (d, *J* = 7.5, H-3); 7.59 (t, *J* = 7.5, H-4)	Unstable
	J = 7.8				

Scheme 2

Ionic reactions typical of aldimines **1a-16a**



ions observed in the spectra. The molecular ion *a* formed is transformed to structure *b*, and then by losing a proton is converted to cation *c*. Structure *c* and its methyl-substituted analogs may be formed only starting from *ortho* isomers (compounds **1a-4a, 13a-16a**). Other isomeric structures (*g*, *h* for the example of compound **5a**) may appear upon primary charge localization on the nitrogen atom of the ring in the azo portion of the aldimine molecule (*f*). The high intensity of the $[M–H]^+$ ion suggests that such transitions are facile.

Quite typical for the spectra of all the aldimines is the presence of peaks for ions formed by losing an HCN group: $[M–HCN]^+$, $[M–HCN–H]^+$, $[M–Me–HCN]^+$, which means high probability of formation of a bond between the hetaryl residues of the aldehyde and the amine. Considering information available in the literature indicating that such fragmentation is absent in the spectra of benzylideneanilines and also anils obtained from 3- and 4-pyridinealdehydes and their derivatives, we may hypothesize that species that have lost HCN arise from molecular ions in which the charge is localized on the nitrogen atom of the ring of the pyridine α-derivatives (in Scheme 2, we give an example of a sequential fragmentation *a* – *d* – *e* for compound **1a**).

In all cases, the $Ar'H^+$ signal has high intensity (especially in spectra of 2-amino-6-methylpyridine derivatives, 100%). Since such a phenomenon was observed previously [15] only in the spectrum of benzylidene-2-aminopyridine, it is presumed that the pyridine ion is formed from the molecular ion (with the charge on the nitrogen atom of the ring of the pyridylaza group) upon addition of the hydrogen of the azomethine group to the pyridine ring. Analogous processes are also typical for aldimines **1a-16a** (Scheme 2, transition *f* – $Ar'H^+$). At the same time, the intensity of the ArH signals is not high, while they are completely absent in the spectra of the 2- and 3-pyridylmethylidene derivatives. This supports the hypothesis given above.

In the spectra of all the aldimines we studied we see $[M–Ar']^+$, Ar^+, $[M–AR]^+$, Ar'^+ signals. It is assumed [5, 15] that the first two arise from molecular ions with the charge on the nitrogen atom of the ring of the pyridylmethylidene group (Scheme 2, ion *i* and Py^+ for the example of compound **1a**). We can analogously assume that $[M–Ar]^+$ and Ar'^+ ions are formed from the molecular ion *f* (Scheme 2, ion *j* and Py^+ for aldimine **1a**). In all cases, the intensity of the Ar'^+ signal is higher than for the Ar^+ signal. This possibly is evidence for a higher probability of charge localization on the nitrogen atom of the ring in the pyridylazo portion of the molecules than on the pyridylmethine group.

It is interesting to compare our results with the only mass spectrum available in the literature for pyridylazopyridylmethine, specifically for 4-pyridylmethylidene-4-aminopyridine [14], *m*/*z* (*I*, %): 183 (100), 182 (35), 156 (1), 155 (2), 105 (16), 79 (17), 78 (29). In that spectrum we see practically none of the fragmentation typical for imines **1a-16a**, due to the presence in the latter of an azomethine group in the *ortho* position of one or both pyridine rings.

X-RAY DIFFRACTION ANALYSIS OF AMINALS 1B AND 6B

With the aim of determining the structure of the novel heterocyclic aminals, in our work we obtained single crystals by crystallization of compounds N,N'-2-pyridylmethylidenebis-2-aminopyridine (**1b**) and N,N'-3-pyridylmethylidenebis-2-amino-3-methylpyridine (**6b**) from a 1:1 benzene–hexane mixture or diethyl ether, respectively, and then studied them by X-ray diffraction. In Figs. 1 and 2 we show three-dimensional models for the molecules of compounds **1b** and **6b** with the labeling of the atoms. In Tables 5 and 6, we give the bond lengths and the bond angles in molecules **1b** and **6b**. Their structures are stabilized by hydrogen bonds: two intermolecular hydrogen bonds for **1b**, and also an intramolecular and intermolecular hydrogen bond for **6b**. The hydrogen bond parameters are given in Table 7.

Owing to the intramolecular bond N(2b)–H(2b···N(1a) in molecule **6b**, one more six-membered ring is formed, N(1a)C(2a)N(2a)C(7)N(2b)H(2b), which has a flattened chair conformation; deviations of the N(1a) and C(7) atoms from the C(2a)N(2a)N(2b)H(2b) plane are equal to 0.692(1) and 0.458(2) Å respectively. The dihedral angle between the average plane of this six-membered ring and the plane of the pyridine ring N(1a)C(2a)···C(6a) is 31.62(6)°. In compound **1b**, the intramolecular hydrogen bond at least is missing in the

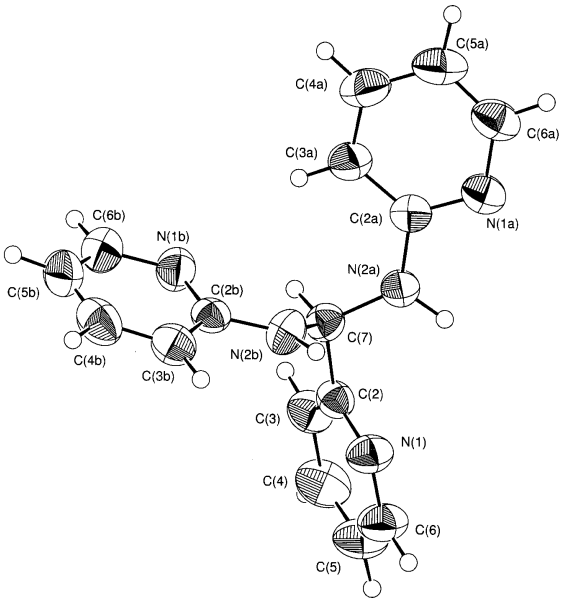


Fig. 1. Three-dimensional model of the molecule for compound **1b**

crystal structure, and accordingly the additional ring is not formed. Therefore, in contrast to **6b**, in molecule **1b** the C(7) atom along with N(2a) lies almost in the plane of the pyridine ring N(1a)C(2a)···C(6a). Analogously, the C(7) and N(2b) atoms are practically coplanar with the plane of the other pyridine ring of molecule **1b**. On the whole, the corresponding bond lengths and bond angles in structures **1b** and **6b** differ insignificantly.

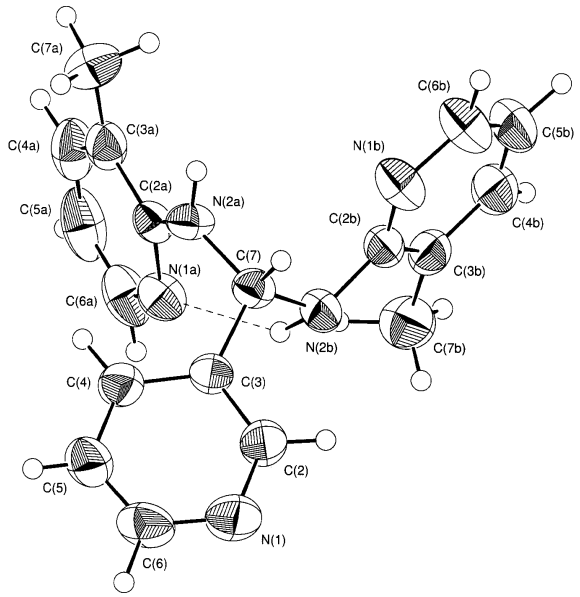


Fig. 2. Three-dimensional model of the molecule for compound **6b**

TABLE 5. Bond Lengths (*d*) in Molecules of Compounds **1b** and **6b**

Bond	*d*, Å		Bond	*d*, Å	
	1b	**6b**		**1b**	**6b**
N(1)–C(2)	1.333(2)	1.335(3)	C(5a)–C(4a)	1.375(3)	1.365(5)
C(2)–C(3)	1.388(2)	1.378(3)	C(6a)–C(5a)	1.360(3)	1.361(5)
C(3)–C(4)	1.385(3)	1.377(3)	N(1a)–C(6a)	1.356(2)	1.346(4)
C(5)–C(4)	1.359(3)	1.383(4)	C(3a)–C(7a)	—	1.486(4)
C(5)–C(6)	1.376(3)	1.351(4)	N(2b)–C(7)	1.458(2)	1.454(3)
N(1)–C(6)	1.339(2)	1.331(4)	C(2b)–N(2b)	1.371(2)	1.394(3)
C(7)–C(2)	1.512(2)	—	C(2b)–N(1b)	1.330(2)	1.323(3)
C(7)–C(3)	—	1.520(3)	C(2b)–C(3b)	1.394(2)	1.404(3)
N(2a)–C(7)	1.449(2)	1.451(3)	C(3b)–C(4b)	1.376(3)	1.378(4)
N(2a)–C(2a)	1.377(2)	1.362(3)	C(4b)–C(5b)	1.369(3)	1.373(5)
C(2a)–N(1a)	1.343(2)	1.335(3)	C(6b)–C(5b)	1.365(3)	1.351(5)
C(2a)–C(3a)	1.398(3)	1.415(3)	N(1b)–C(6b)	1.350(3)	1.345(3)
C(4a)–C(3a)	1.362(3)	1.371(4)	C(3b)–C(7b)	—	1.492(4)

TABLE 6. Bond Angles (θ) in Molecules of Compounds **1b** and **6b**

Angle	θ, deg		Angle	θ, deg	
	1b	**6b**		**1b**	**6b**
C(7)–N(2a)–C(2a)	122.68(14)	123.2(2)	N(1)–C(2)–C(7)	115.70(15)	
N(2b)–C(2b)–N(1b)	118.51(15)	116.7(2)	C(2a)–C(3a)–C(4a)	118.9(2)	116.8(3)
C(3)–C(2)–N(1)	122.6(2)	116.7(2)	C(2a)–C(3a)–C(7a)		121.3(2)
N(2b)–C(2b)–C(3b)	119.3(2)	116.7(2)	C(7)–C(2)–C(3)	121.7(2)	
N(2a)–C(7)–N(2b)	112.20(14)	114.7(2)	C(4a)–C(3a)–C(7a)		121.9(3)
N(1b)–C(2b)–C(3b)	122.2(2)	123.6(2)	C(2b)–C(3b)–C(4b)	118.7(2)	116.2(3)
N(2a)–C(7)–C(3)		113.6(2)	N(1a)–C(6a)–C(5a)	124.3(2)	124.0(3)
C(2b)–N(2b)–C(7)	123.6(2)	118.9(2)	N(1b)–C(2b)–C(3b)		123.6(2)
N(2b)–C(7)–C(3)		109.5(2)	N(1b)–C(6b)–C(5b)	124.0(2)	123.7(3)
C(2b)–N(1b)–C(6b)	117.3(2)	117.4(2)	N(2b)–C(2b)–C(3b)		116.7(2)
C(2)–N(1)–C(6)	117.8(2)	116.5(2)	C(6a)–C(5a)–C(4a)	118.2(2)	118.5(3)
C(2a)–N(1a)–C(6a)	116.4(2)	116.7(2)	C(6)–C(5)–C(4)	118.8(2)	119.6(3)
N(2a)–C(7)–C(2)	107.49(13)		C(2b)–C(3b)–C(7b)		121.4(2)
N(2a)–C(2a)–N(1a)	115.2(2)	117.2(2)	C(5a)–C(4a)–C(3a)	119.8(2)	120.7(3)
N(2b)–C(7)–C(2)	110.66(13)		C(4b)–C(3b)–C(7b)		122.5(2)
N(2a)–C(2a)–C(3a)	122.4(2)	119.6(2)	C(3b)–C(4b)–C(5b)	119.6(2)	121.0(3)
N(1a)–C(2a)–C(3a)	122.4(2)	123.2(2)	C(3)–C(4)–C(5)	119.6(2)	119.0(2)
C(2)–C(3)–C(7)		120.0(2)	C(6b)–C(5b)–C(4b)	118.1(2)	118.1(3)
C(2)–C(3)–C(4)	118.2(2)	116.7(2)	N(1)–C(6)–C(5)	123.1(2)	123.1(2)
C(7)–C(3)–C(4)		123.2(2)			

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian mercury spectrometer (200 MHz) in $CDCl_3$, DMSO-d_6, or C_6D_6, internal standard TMS. The mass spectra were obtained on an HP 6890 GC/MS chromatomass spectrometer, equipped with an HP-5 MS capillary column (30.0 m × 250 μm × 0.25 μm), with temperature

TABLE 7. Hydrogen Bond Parameters in Structures **1b** and **6b**

Hydrogen bond D–H···A*	D···A, Å	D–H, Å	H···A, Å	D–H···A, deg	Position of A atom
		Molecule **1b**			
N(2A)–H(2A)···N(1B)	3.241(2)	0.84(1)	2.43(1)	162(1)	$-x, y, 1/2 - z$
N(2B)–H(2B)···N(1)	3.139(2)	0.84(1)	2.30(1)	176(1)	$-x, y, 1/2 - z$
		Molecule **6b**			
N(2A)–H(2A)···N(1)	3.062(2)	0.91(1)	2.21(1)	157(1)	$x, 1/2 - y, 1/2 + z$
N(2B)–H(2B)···N(1A)	2.814(2)	1.03(1)	1.98(1)	136(2)	x, y, z

* D is the donor atom. A is the acceptor atom.

programming from 70 to 260°C (10°C/min). The benzene was distilled over CaH_2 before use. The reagents used in the work were obtained from the companies Fluka, Merck, and Acros. The pyridinealdehydes were purified by vacuum distillation while the 2-aminopyridines were recrystallized from benzene, after which their properties matched literature data. In this work, we used 4A molecular sieves (VEB Laborchemie Apolda).

X-ray Diffraction Studies. Colorless single crystals of compounds **1b** and **6b** were obtained by slow crystallization from a 1:1 benzene–hexane mixture or diethyl ether respectively. The structure studies were performed at 25°C on a Nonius KappaCCD automatic diffractometer (MoKα radiation, 2θmax 55°). The basic crystallographic data and also the parameters for deciphering and refinement of the structures are given in Table 8. The structures were deciphered by direct methods using the programs in [27, 28] and least-squares refined in the full-matrix anisotropic approximation [29]. The coordinates of the non-hydrogen atoms and their equivalent isotropic thermal parameters are given in Tables 9 and 10.

TABLE 8. Crystallographic Data for Compounds **1b** and **6b**

Characteristics	Compound	
	1b	**6b**
Formula	$C_{16}H_{15}N_5$	$C_{18}H_{19}N_5$
Molecular weight	277.331	305.385
Color	Colorless	Colorless
Size, mm	0.15×0.20×0.30	0.25×0.25×0.40
Crystal syngony	Rhombic	Monoclinic
Space group	*P bcn*	*P* $2_1/c$
Lattice parameters		
a, Å	16.8731(4)	13.8177(9)
b, Å	8.6875(2)	8.9000(5)
c, Å	19.6167(7)	13.2056(6)
β, degrees	90.0(0)	93.704(2)
Unit cell volume, *V*, Å^3	2875.5(1)	1620.6(2)
Number of molecules per unit cell, *Z*	8	4
Density (calculated), *d*, g/cm^3	1.281	1.252
Absorption coefficient, μ, mm^{-1}	0.08	0.08
Number of independent reflections	3758	3541
Number of reflections with $I > 2\sigma(I)$	1695	2096
Number of refined parameters	190	244
R factor	0.055	0.049

TABLE 9. Coordinates of Non-hydrogen Atoms and Their Thermal Parameters in the **1b** Molecule

Atom	*x*	*y*	*z*	U_{eq}
N(1)	0.42439(13)	0.2148(2)	0.20624(12)	0.0583(12)
C(2)	0.45328(13)	-0.1918(3)	0.14382(14)	0.0469(12)
C(3)	0.45919(16)	-0.3088(3)	0.09594(15)	0.0606(15)
C(4)	0.43602(19)	-0.4556(3)	0.1149(2)	0.0773(19)
C(5)	0.40909(19)	-0.4810(3)	0.1792(2)	0.0755(18)
C(6)	0.40374(18)	-0.3584(3)	0.22342(17)	0.0680(17)
C(7)	0.47900(13)	-0.0289(3)	0.12800(13)	0.0484(13)
N(1a)	0.65064(12)	0.1558(2)	0.20673(12)	0.0570(12)
C(2a)	0.59426(14)	0.1332(3)	0.15947(14)	0.0483(13)
C(3a)	0.58264(16)	0.2344(3)	0.10499(16)	0.0618(15)
C(4a)	0.63113(19)	0.3589(3)	0.09881(18)	0.0711(18)
C(5a)	0.68991(18)	0.3835(3)	0.14615(18)	0.0704(18)
C(6a)	0.69760(16)	0.2810(3)	0.19810(17)	0.0653(16)
N(2a)	0.54893(12)	0.0030(2)	0.16844(12)	0.0544(11)
N(1b)	0.39518(13)	0.1429(2)	0.02821(12)	0.0587(13)
C(2b)	0.36869(13)	0.1438(2)	0.09206(14)	0.0454(12)
C(3b)	0.29707(15)	0.2128(3)	0.11006(16)	0.0588(15)
C(4b)	0.25470(17)	0.2896(3)	0.06070(19)	0.0696(17)
C(5b)	0.28199(17)	0.2919(3)	-0.0050(2)	0.0730(18)
C(6b)	0.35075(18)	0.2154(4)	-0.01914(16)	0.0720(18)
N(2b)	0.41499(13)	0.0793(2)	0.14187(11)	0.0545(12)

TABLE 10. Coordinates of Non-hydrogen Atoms and Their Thermal Parameters in the **6b** Molecule

Atom	*x*	*y*	*z*	U_{eq}
N(1)	0.12801(17)	0.2435(3)	0.41772(15)	0.0677(12)
C(2)	0.18138(18)	0.2241(3)	0.33799(17)	0.0572(12)
C(3)	0.15682(14)	0.1320(2)	0.25647(14)	0.0414(9)
C(4)	0.07218(16)	0.0512(3)	0.26030(16)	0.0528(11)
C(5)	0.01641(19)	0.0694(4)	0.3427(2)	0.0657(14)
C(6)	0.04586(18)	0.1655(3)	0.41769(18)	0.0645(14)
C(7)	0.21855(15)	0.1311(2)	0.16525(14)	0.0420(9)
N(1a)	0.24153(14)	0.1793(2)	0.17307(13)	0.0517(10)
C(2a)	0.20405(14)	-0.1207(2)	0.08613(14)	0.0410(9)
C(3a)	0.18466(16)	-0.2064(3)	-0.00311(17)	0.0521(11)
C(4a)	0.2100(2)	-0.3554(3)	0.0015(3)	0.0675(15)
C(5a)	0.2504(2)	-0.4164(3)	0.0891(3)	0.0771(17)
C(6a)	0.26364(19)	-0.3265(3)	0.1723(2)	0.0659(14)
N(2a)	0.18347(13)	0.0291(2)	0.08546(13)	0.0439(8)
C(7a)	0.1371(2)	-0.1385(4)	-0.0963(2)	0.0780(17)
N(1b)	0.36759(15)	0.2487(2)	0.06266(16)	0.0604(11)
C(2b)	0.39126(16)	0.1481(2)	0.13379(15)	0.0448(10)
C(3b)	0.48389(16)	0.0838(3)	0.14811(17)	0.0512(11)
C(4b)	0.55190(18)	0.1325(4)	0.08368(19)	0.0650(14)
C(5b)	0.5292(2)	0.2393(4)	0.0110(2)	0.0745(16)
C(6b)	0.4377(2)	0.2936(3)	0.0033(2)	0.0745(16)
N(2b)	0.31991(13)	0.1110(2)	0.19940(12)	0.0473(9)
C(7b)	0.5061(2)	-0.0319(4)	0.2280(2)	0.0713(17)

General Procedure for Synthesis of Azomethines 1a-16a. Dry benzene (10 ml) were placed into a flask along with each of the starting aldehyde and amine (5 mmol), then freshly calcined molecular sieves (5 g); this was boiled with a reflux condenser under argon on a water bath for 5 h. After such treatment, practically complete conversion of the starting aldehyde and amine occurred and the corresponding aldimine was formed, evidence for which came from GLC-MS analysis data for the reaction mixtures. At the end of the reaction, the sieve was filtered off and washed with benzene, the filtrate was evaporated off under reduced pressure at 40°C (15 mm), and the slight residues of the starting materials were removed under vacuum at 45-50°C (0.1 mm). The products obtained were crystalline compounds (light yellow or white). Their characteristics (Tables 1-3) correspond to the proposed structure.

Synthesis of Aminals 5b-7b, 14b, 16b. Dry benzene (10 ml), the starting aldehyde (5 mmol), and the amine (10 mmol) and then freshly calcined molecular sieves (5 g) were placed into a flask. The reactions were carried out at room temperature for 20 h. The precipitates formed were separated from the sieves (**6b, 14b, 16b** were additionally purified with ether or benzene). The compounds were obtained in 49% to 58% yield.

Synthesis of Aminals 1b-4b. No precipitation occurred after carrying out the condensation reaction at 20°C for 20 h. The sieve was filtered out, and the filtrate was held at room temperature for another 48 h. The precipitates formed were filtered out and purified with ether, and the aminals were obtained in 56 to 67% yield.

Synthesis of Aminal 8b. The reaction was carried out as indicated above, and then the mixture was boiled for 5 h. After cooling and holding in a refrigerator, the precipitate formed was purified with ether and hexane (yield 45%).

Synthesis of Aminals 9b-12b. Condensations were carried out in a cryostat at a temperature of 15°C (40 h). After removal of the sieves and evaporation of the benzene, the **11b, 12b** formed were purified with ether. The precipitates obtained in synthesis of **9b** and **10b** were dissolved in benzene and held at room temperature for 60 h. Then they were evaporated down and **9b** was purified with ether, while **10b** was purified with ether and hexane.

Synthesis of Aminals 13b, 15b. Dry benzene (10 ml), aldehyde **4** (5 mmol), and amine (5 mmol) and then freshly calcined molecular sieves (5 g) were placed into a flask. The reactions were carried out at room temperature for 20 h. The precipitates formed were filtered out and separated from the sieves.

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