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Heteroaromatic Primary Amines and Formaldehyde: the Formation of N-Hydroxymethyl Derivatives

Giancarlo Verardo, Fausto Gorassini, Angelo G. Giumanini,* Tiziano Scubla, Marilena Tolazzi and Paolo Strazzolini

Department of Chemical Sciences and Technologies, University of Udine, I-33100 Udine, Italy

Abstract: A product study of the reaction of three heteroaromatic primary amines with paraformaldehyde was made: N-hydroxymethylamines were identified in all cases. Two of them yielded also N,N-dihydroxymethyl derivatives. X-Ray diffraction structure determination on one of the N-hydroxymethyl derivatives ruled out the presence of internal hydrogen bonding in the solid state, notwithstanding the almost ideally planar arrangement of the aromatic moiety and the amino function.

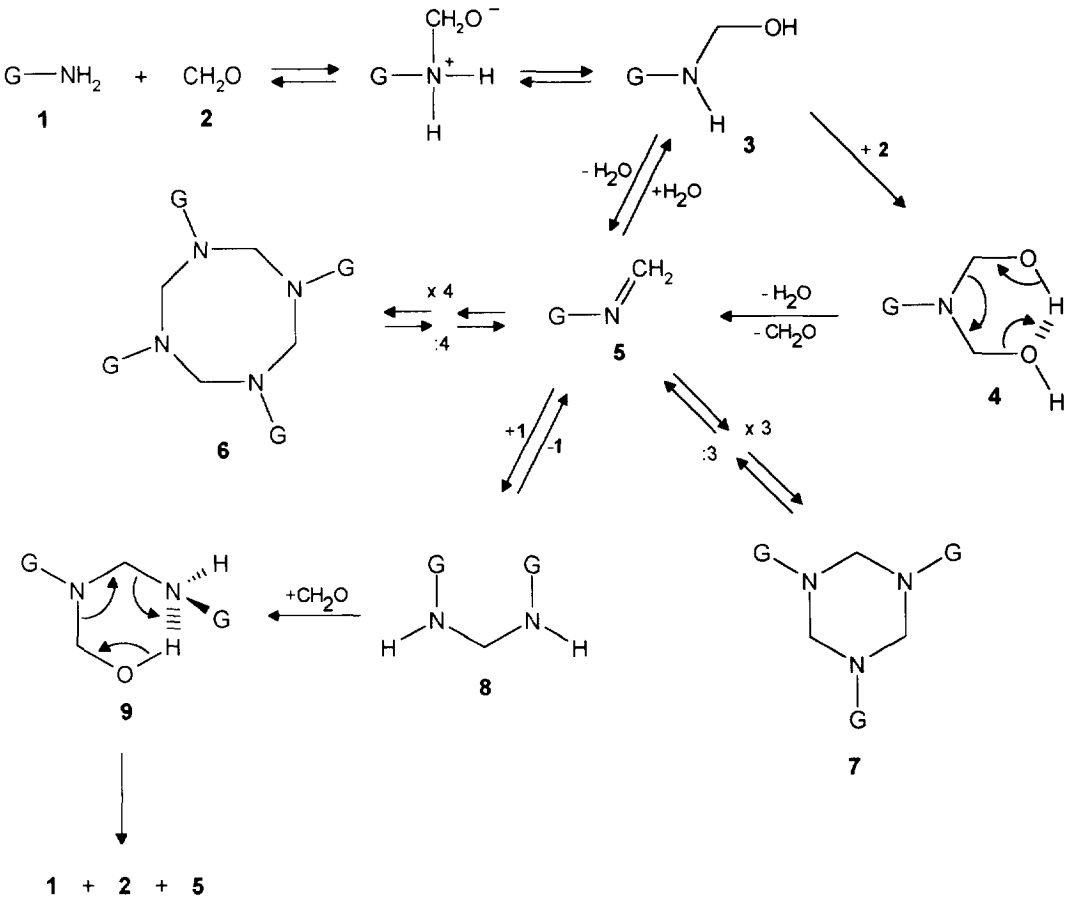
N-Hydroxymethylamines **3** from primary amines **1** and formaldehyde **2** are generally indicated as the reaction intermediates[1] on the way to the anhydro products **5**,[2] which eventually oligomerize to trimers **7** and tetramers **6** in reversible processes (Scheme 1).[3] In slightly basic or neutral solution these aminols are believed to be able to pick up a second molecule of formaldehyde[1d,4] yielding the corresponding N,N-dihydroxymethyl **4**. Compounds **4** could actually be more likely intermediates on the way to imines **5** through cyclic six membered transition states; the intermediates **3**, though, are seldom, if ever, observed, a fact to be related to the fast reactions following this rate determing step. The literature about the reaction of heteroaromatic primary amines with formaldehyde is very scant: Carpignano's group studied the three pyridylamines and described[1d,5] derivatives of the type **3**, **4**, **7** and **8** (Scheme 1); another work[6] involved some 2-aminopyrimidines and a 2-amino-1,3,5-triazine; the former yielded products of the type **3** and **8**, the latter appeared unreactive.

The aim of this report is to give definitive structural evidence for the identification of N-hydroxymethyl-2--aminopyrimidine (**3a**) and its actual conformation and solid state structure, as well as relate about the preparation of **3b** and **4b** from 2-amino-1,2,4-triazine (**1b**) and **3c** and **4c** from 2-amino-5-nitropyrimidine (**1c**).

RESULTS AND DISCUSSION

We have reproduced the N-hydroxymethylamine **3a** according to our dry method[7] using paraformaldehyde (PF) in hot toluene on 2-aminopyrimidine (**1a**).

Scheme 1



The ^{1}H NMR and electron impact (70 eV) MS spectra of product **3a** are shown in Figures 1 and 2, respectively. Compound **3a** could be easily recrystallized from boiling toluene without decomposition, showing an unexpected thermal stability; solutions in refluxing chloroform exhibited analogous stability. The mass spectrum was obtained by evaporating the pure solid into an ion source of a mass spectrometer at 50°C. Beside the parent ion **10a** showing up at m/z 125, loss of OH and H_2O were observed (m/z 108 and 107, respectively); subsequent loss of HCN from the ion at m/z 107 yielded m/z 80. Before ionization, either in the vaporization process or during the collision with the hot surfaces of the ionization chamber, **3a** may partly revert to **1a** (95 u) and **2** (30 u), which are largely represented in the mass spectrum. If this were the prevalent process, the molecules of **1a** would yield the spectral pattern of the ionized amine,[8] where the cherged fragment at m/z 52

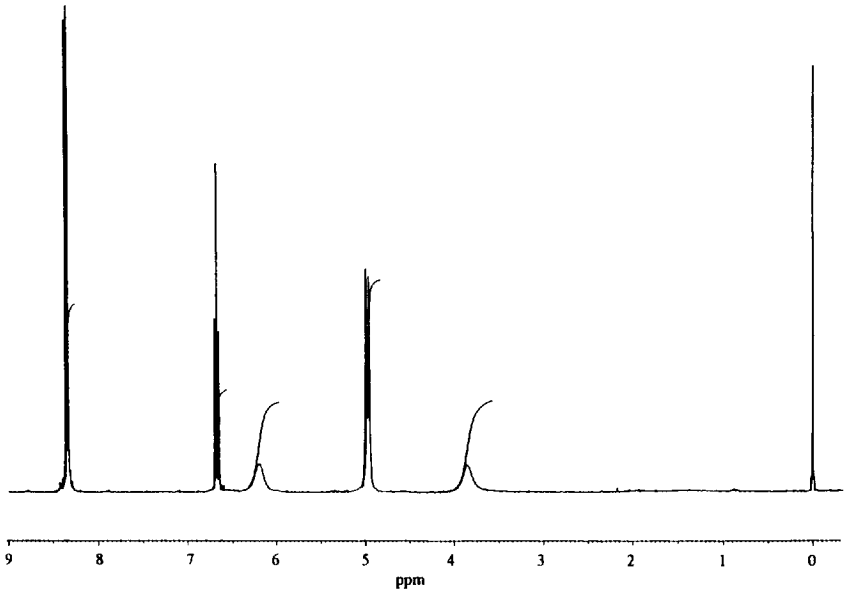


Fig. 1. ^{1}H NMR spectrum of N-hydroxymethyl-2-aminopyrimidine (**3a**) in $CDCl_3$

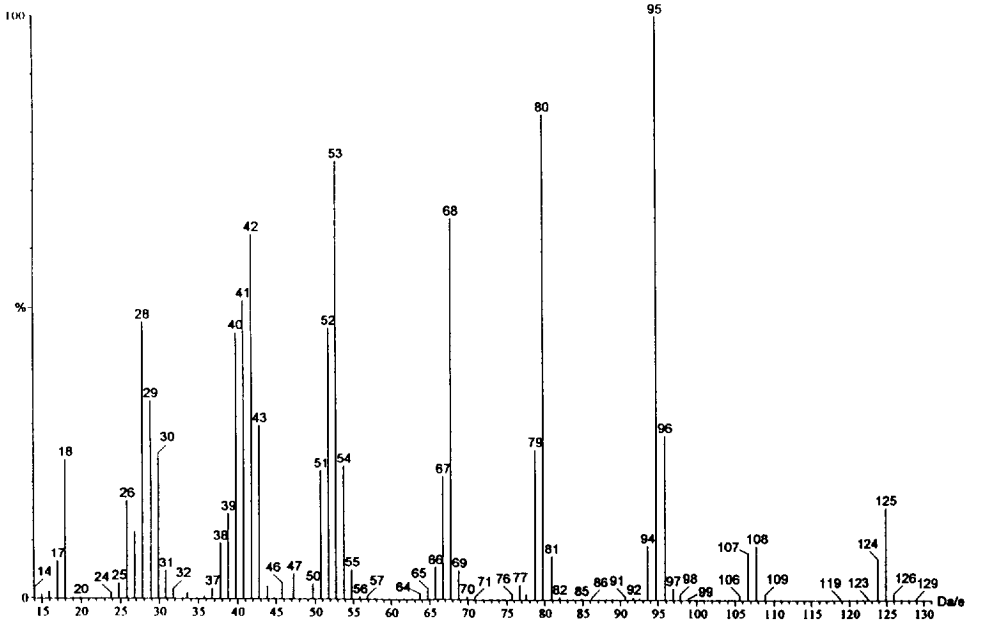
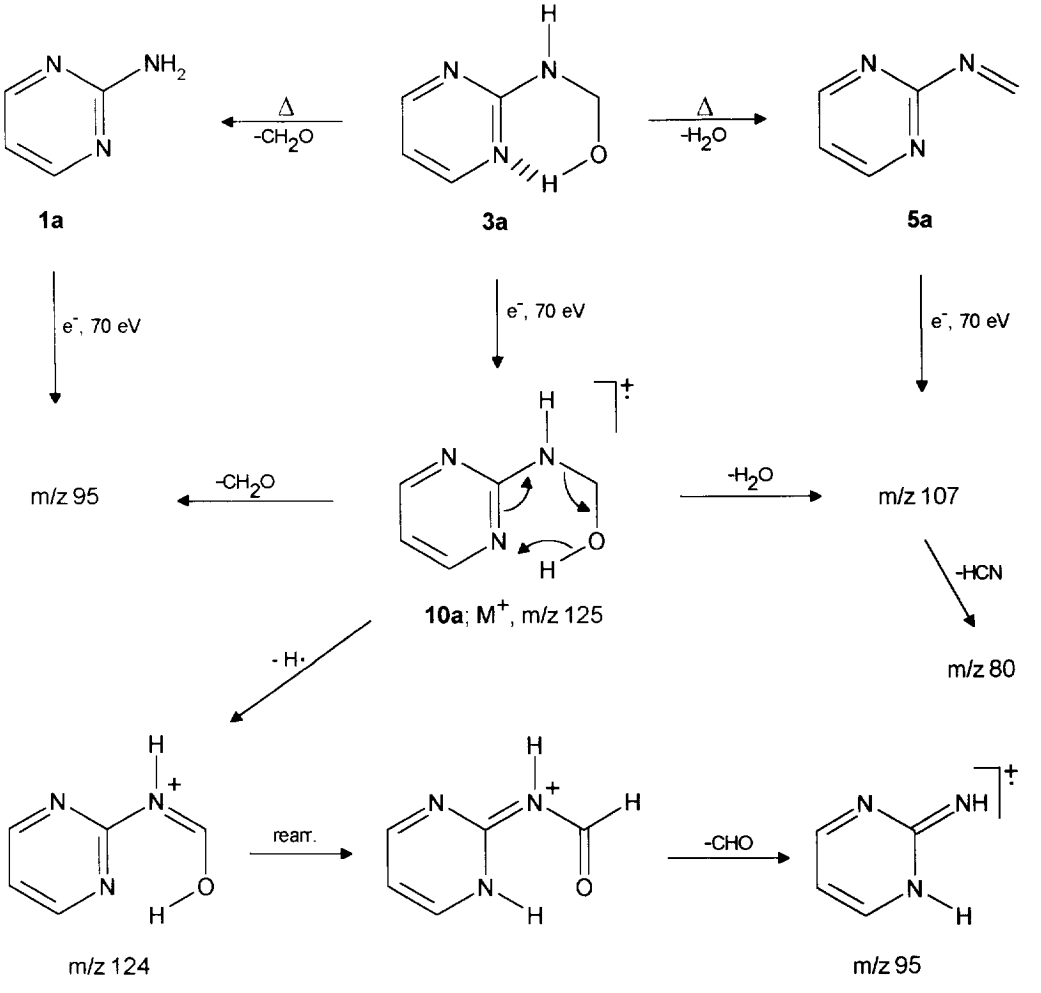


Fig. 2. Mass spectrum of N-hydroxymethyl-2-aminopyrimidine (**3a**)

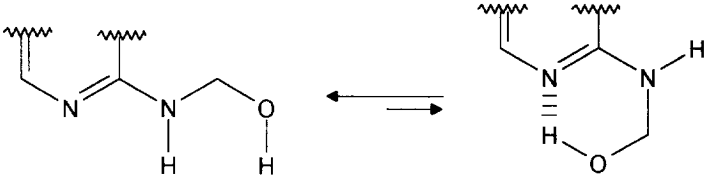
(H_2N–CN^+) is by far the most intense peak. This is not the case, therefore, at least a good part of the intact molecules **3a** ionized to **10a** which eventually broke down to the observed ions. Extensive losses of HCN are, as expected, noticeable all over the spectrum (Scheme 2).

Scheme 2



The ^{1}H NMR pattern of **3a** could be easily reconciled with the structure of N-hydroxymethylamine. The proton on the nitrogen atom showed a peak at 6.19 ppm in the form of a broad singlet at room temperature. At -30°C the doublet of the methylene resonance became more similar to a poorly resolved triplet, the shape of

other peaks remaining unchanged. The observation was rationalized as an increased coupling with some definite conformation of the NH, a fact in turn attributed to the preferential freezing of a single conformation by rotation about the ar–C–N bond. The hydroxyl band signal, also a broad singlet, which was unaltered by lowering the temperature, was found at 3.85 ppm, a location in agreement with expectation. The fact that the OH is a singlet may be due to a fast exchange with other solute molecules. The positions of the several chemical shifts were practically unchanged changing the solvent from chloroform-*d* to acetonitrile-d_3. The chemical shift of the OH and its moltiplicity, now a triplet, was consistent with a loosely moving OH (structure **11**), rather then an internally hydrogen bonded one (structure **12**).



11 **12**

The latter attractive hypothesis was definitively ruled out by the aromatic pattern shown by the NMR spectrum of **3a**, indicating the presence of two chemically equivalent protons. The ^{13}C NMR spectrum reinforced these arguments.

X-Ray diffraction structural determination (Table 1 and Figure 3) of solid **3a** also showed the reluctance of this compound to yield internal hydrogen bridges. Whereas the ring appeared ideally aromatic with a perfect planarity and the shape of the ring was that of a very regular hexagon; the nitrogen atom and the methylol carbon laid in the plane of the ring, with a ar–CN bond distance strongly suggestive of an important π bond contribution. This enhanced conjugation with respect to the case of normal aromatic amines, showing variable degrees of pyramidality at the amino nitrogen[9] was already observed in a study of 4-dimethylaminopyridine.[10] The oxygen atom pointed definitively away from the ring to which it was linked through covalent bonds to yield its proton for a hydrogen bridge with the N(1)' atom, a repetive feature of the solid state arrangement of the molecules of **3a**. The N(1)'–H–O(1) bond length (2.88 Å) indicated a quite normal type of hydrogen bonding.

Whereas 2-amino-1,3,5-triazine was found unreactive with aqueous formaldehyde, 3-amino-1,2,4-triazine (**1b**) reacted with PF in boiling toluene to yield both the corresponding N-aminol **3b** and its N,N-dihydroxymethyl derivative **4b** under all the different conditions we tested. Slight changes in the experimental procedures allowed the separation of **3b** and **4b** from the reaction mixtures as very pure solids. The ^1H NMR spectra of **1b**, **3b** and **4b** exhibited identical patterns for the aromatic protons and ideally located for quantitative evaluation of

Table 1. Molecular Dimensions for N-Hydroxymethyl-2-aminopyrimidine (**3a**) not Involving Hydrogen Atoms.

Bond Lenghts (Å)		Bond Angles (°)		Torsion Angles (°)	
O(1)-C(5)	1.408(8)	C(1)-N(1)-C(4)	115.4(5)	C(1)-N(1)-C(4)-C(3)	-0.9(0.9)
N(1)-C(1)	1.348(7)	C(1)-N(2)-C(2)	115.9(5)	C(4)-N(1)-C(1)-N(2)	1.4(0.9)
N(1)-C(4)	1.330(8)	C81)-N(3)-C(5)	124.1(5)	C(4)-N(1)-C(1)-N(3)	-179.8(0.5)
N(2)-C(1)	1.332(7)	C(4)-C(3)-C(2)	116.6(6)	C(2)-N(2)-C(1)-N(1)	-0.8(0.9)
N(2)-C(2)	1.336(8)	N(2)-C(1)-N(3)	118.4(5)	C(1)-N(2)-C(2)-C(3)	-0.4(0.9)
N(3)-C(1)	1.352(8)	N(1)-C(1)-N(3)	115.5(5)	C(2)-N(2)-C(1)-N(3)	-179.6(0.5)
N(3)-C(5)	1.434(8)	N(1)-C(1)-N(2)	126.1(5)	C(1)-N(3)-C(5)-O(1)	-79.6(0.7)
C(3)-C(4)	1.361(10)	N(1)-C(4)-C(3)	123.4(6)	C(5)-N(3)-C(1)-N(2)	-4.1(0.8)
C(3)-C(2)	1.376(9)	O(1)-C(5)-N(3)	113.8(5)	C(5)-N(3)-C(1)-N(1)	176.9(0.5)
		N(2)-C(2)-C(3)	122.6(6)	C(4)-C(3)-C(2)-N(2)	0.8(1.0)
				C(2)-C(3)-C(4)-N(1)	-0.1(1.0)

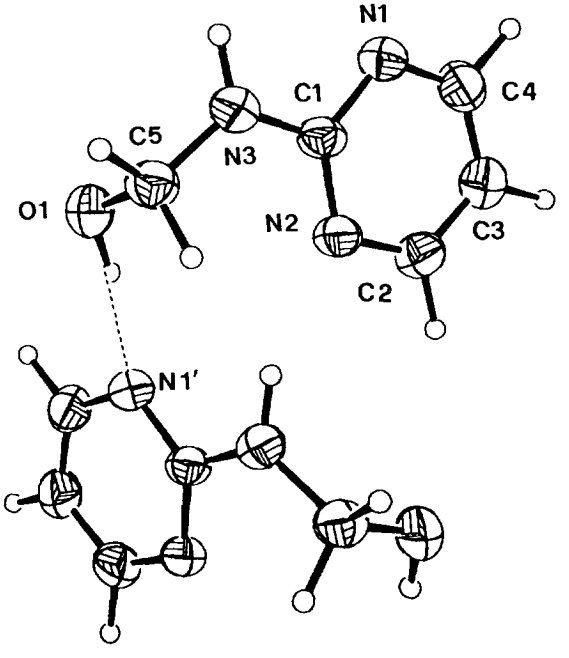
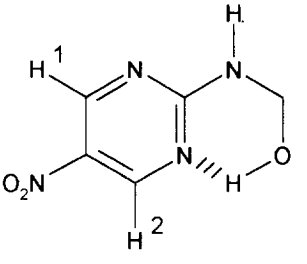


Fig. 3. An ORTEP view of the structure and packing of solid N-hydroxymethyl-2-aminopyrimidine (**3a**)

relative concentrations of the three substances in mixtures. Each component **3b** and **4b** appeared to be represented only by a simple aromatic pattern, an indication of the presence of a single (or rapidly interchanging) conformer. The increasing ring electronegativity seemed to be reflected by a shift to lower field of the broad resonance of the amino proton of **3b**, which induced splitting of the methylene group, which was under a similar influence from the hydroxyl proton, as could be established by the suitable decoupling experiments. As a result of these reciprocal effects the methylene protons of **3b** appeared as a pseudo-triplet, whereas the OH group showed up as a triplet at relatively low field. The appearance of this splitting at lower field than for **3a** might be interpreted as due to some internal hydrogen bonding formation. Decreasing hydrogen bonding is known to shift the proton resonance upfield.[11]

Diol **4b** exhibited a general downfield shift of the proton resonances in comparison with analogous protons both in **1b** and **3b**. Thus, the single doublet for the methylene protons was found at 5.30 ppm in acetone-d_6: the methylenes appeared equivalent, therefore ruling out the existence of any permanent strong internal hydrogen bonding. Consistently, the hydroxyl groups protons appeared as a broad triplet, which became a singlet when the methylene protons were irradiated.

5-Nitro-2-aminopyrimidine (**1c**) upon reaction with PF in boiling toluene gave a mixture of N-hydroxymethyl and N,N-dihydroxymethyl amines (**3c** and **4c**) beside unreacted substrate, as shown by ^{1}H NMR on the intact reaction mixture from which the solvent was removed in vacuo. The integral values for the observed peaks revealed an aromatic AB quartet centered at 9.09 ppm to **3c**, a piece of evidence for the non equivalence of the aromatic protons, induced by a strong internal hydrogen bond (**3c'**).



3c'

The hydroxyl proton showed up as a well resolved triplet, the methylene protons were represented by a pseudo-triplet and the NH group as a wide singlet. The aromatic pattern was therefore at variance with our previous observation on systems **3a** and **3b** and perhaps also with that of the diol **4c**, whose aromatic protons generated a singlet at lower fields (9.16 ppm). In the latter case it cannot be ruled out that both side chains were

symmetrically engaged in hydrogen bonds with the heterocycle's nitrogens. The methylene groups of **4c** were represented by a sharp doublet, which also ruled out non symmetric structures. Once more the hydroxyl protons appeared as a sharp triplet.

Silylation of the mixture **1c-3c-4c** by trimethylchlorosilane (TMCS) gave the N-trimethylsilylpyrimidine (**13**), the O-trimethylsilyl derivative **14** of **3c** and the O,O'-bis(trimethylsilyl) derivative **15** of **4c**, which were amenable to GC-MS analysis. The mass spectra obtained were consistent with the structures elucidated by NMR spectroscopy.

EXPERIMENTAL SECTION

Materials. Amines **1a-c** were purchased from Aldrich, Milan, Italy. trimethylchlorosilane (TMCS) and paraformaldehyde (PF) were obtained from BDH, Italy.

Instruments and Methods. Elemental analyses were performed with a Carlo Erba Mod. 1106 elemental analyzer and were in satisfactory agreement with calculated values. GC analyses were performed with a FISONS-Trio 2000 gaschromatograph-mass spectrometer, working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 260°C and the column (Supelco SE 54, 30 m, 0.32 mm i.d., coated with a 0.25 μm phenyl methyl silicone rubber film) temperature was programmed from 80°C to 300°C with a gradient of 10°C/min. Direct inlet MS spectra were obtained on the same instrument: temperatures between 50 and 200°C were found suitable to volatilize all the compounds into the ion source. The actual spectra were recorded by vaporization (50-80°C) at constant temperature. This process was continued until no more product evapora-ted, then the temperature was raised up to 300°C in order to observe any other possible coproduct initially present or formed during the vaporization, but none was thus detected. Continuous monitoring of the evaporate by MS allowed to ascertain the steady nature of the spectral features during the evaporation, an indication of the homogeneity of the original samples and of the fact that any decomposition during the evaporation could be ruled out.

^{1}H NMR spectra were recorded with a Bruker AC-F 200 operating at 200 MHz using TMS as internal standard.^{13}C NMR spectra were recorded at 50 MHz. Due to the low solubility of some products in chloroform-*d* complementary spectra were recorded also in acetone-d_6 and acetonitrile-d_3.

Infrared spectra (IR) of all solids were recorded with the KBr technique on a Nicolet Magna FT-IR 550.

Melting points were determined with an automatic Mettler (mod. FP61) apparatus and are not corrected.

X-Ray Diffraction Data Collection and Structural Analysis. 1470 reflections were measured on a CAD-4 diffractometer with ω-scan in the range $6 < 2\theta < 48°$ (+-h,k,l octants; max hkl values 5,21,11): of these 630

were considered observed having $I > 3\sigma(I)$. The structure was solved with SIR92[12] and refined with Shelx76.[13] The weighting scheme for last cycles was $w = 3.57/[\sigma^2(F) + 0.00075\ F^2]$.

Crystal Data. Formula weight = 125.13, monoclinic, $P2_1/c$, a = 4.235(3), b = 16.349(3), c = 8.886(1) Å, β = 98.87(1)°. V = 607.9 Å^3, Z = 4, D_x = 1.37 Mgm^{-3}. λ(MoKα) = 0.71069 Å, μ = 0.94 cm^{-1}, F(000) = 264, room temperature, crystal dimensions 0.2 x 0.4 x 0.3 mm, R = 0.0462 (R_w = 0.0549) with 84 refinable parameters, maximum shift/error ratio equal to 0.4. The maximum residual electronic density was 0.21 electron/Å^3.

*Reaction of 2-aminopyrimidine (**1a**) with PF*. To the amine **1a** (1.00 g, 10.5 mmol) in refluxing toluene (20 mL) PF (0.38 g, 12.7 mmol) was added portionwise during 10 min and refluxed for additional 60 min. Excess PF was removed by filtration of the cold solution. Concentration of the solution caused the separation of solid **3a** (yield: 82%). Large white needles may be obtained by recrystallization from hot toluene: mp 122°C, lit[6] 110-112°C; IR (KBr) 3225s, 1600vs, 1530vs, 1500vs, 1470vs, 1450vs, 1410s, 1380vs, 1240vs, 1110vs, 1090s, 1060vs, 1010vs, 970s, 800vs, 740s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (broad s, 1H, OH), 4.97 (d, *J* = 6.8 Hz, 2H, CH_2), 6.19 (broad s, 1H, NH), 6.67 (t, *J* = 4.8 Hz, 1H, ar-H), 8.33 (d, *J* = 4.8 Hz, 2H, ar-H); ^{1}H NMR ($CDCl_3$ at -30°C) δ 4.23 (broad s, 1H, OH), 5.00 (overlapping broad dd showing as a broad t, *J* = 6.4 Hz, 2H, CH_2), 6.40 (broad s, 1H, NH), 6.73 (t, *J* = 4.9 Hz, 1H, ar-H), 8.38 (d, *J* = 4.9 Hz, 2H, ar-H); ^{1}H NMR (CD_3CN) δ 3.82 (t, *J* = 7.0 Hz, 1H, OH), 4.84 (overlapping dd showing as a t, *J* = 7.0 Hz, 2H, CH_2), 6.56 (broad s, 1H, NH), 6.67 (t, *J* = 4.8 Hz, 1H, ar-H), 8.31 (d, *J* = 4.8 Hz, 2H, ar-H); ^{1}H NMR (CD_3CN and D_2O) δ 4.87 (s, 2H, CH_2), 6.77 (t, *J* = 4.9 Hz, 1H, ar-H), 8.33 (d, *J* = 4.9 Hz, 2H, ar-H); ^{13}C NMR ($CDCl_3$) δ 66.7, 112.1, 158.2, 161.8; MS m/z 125(M^+, 17), 124(7), 108(10), 107(9), 96(29), 95(100), 80(85), 79(26), 68(67), 67(22), 54(24), 53(77), 52(48), 43(31), 42(64). Anal. Calcd for $C_5H_7N_3O$: C, 47.99; H, 5.64; N, 33.58. Found: C, 47.90; H, 5.61; N, 33.54.

*Reaction of 3-amino-1,2,4-triazine (**1b**) and PF*. A.- The amine **1b** (1.00 g, 10.4 mmol) and PF (0.34 g, 11.4 mmol) in toluene (20 mL) were refluxed during 1 h to obtain a clear colorless solution. Evaporation of the solvent under reduced pressure gave a solid, which contained three components, namely unreacted amine **1b** (30%), its N-hydroxymethyl derivative **3b** (58%) and its N,N-dihydroxymethyl derivative **4b** (12%), as determi-ned on the basis of the ^{1}H NMR spectrum of the intact mixture.

B.- The above reaction was repeated in acetonitrile at 60°C during 2 d to obtain a clear solution. The reaction mixture was also found to contain **1b**, **3b** and **4b**, but **3b** was the main product (80%). Recrystallization of the solid residue from toluene yielded (20%) pure crystalline **3b**: mp 112°C; IR (KBr) 3338vs, 3286vs, 1559vs, 1534vs, 1515vs, 1458s, 1402s, 1358s, 1289s, 1117s, 1041vs, 1016vs, 957s, 808s,

595m cm^{-1}; ^1H NMR (acetone-d_6) δ 4.76 (t, J = 6.9 Hz, 1H, OH), 5.03 (overlapping dd showing as a t, J = 6.8 Hz, 2H, CH_2), 7.59 (broad s, 1H, NH), 8.27 (d, J = 2.3 Hz, 1H, ar-H), 8.66 (d, J = 2.3 Hz, 1H, ar-H); ^1H NMR (CD_3CN) δ 3.92 (t, J = 6.7 Hz, 1H, OH), 4.93 (overlapping dd showing as a t, J = 6.8 Hz, 2H, CH_2), 6.89 (broad s, 1H, NH), 8.23 (d, J = 2.3 Hz, 1H, ar-H), 8.63 (d, J = 2.3 Hz, 1H, ar-H); MS m/z 126(M^+, 22), 109(24), 108(14), 99(14), 98(16), 96(77), 80(29), 72(24), 68(38), 54(28), 53(36), 43(50), 42(100), 41(80). Anal. Calcd for $C_4H_6N_4O$: C, 38.09; H, 4.79; N, 44.42. Found: C, 38.11; H, 4.80; N, 44.42.

C.- Reaction A was performed with a triple amount of PF (1.14 g, 38.0 mmol): concentration of the reaction mixture under reduced pressure gave a solid which contained **1b**, **3b** and **4b**, but **4b** was the main product (80%). Recrystallization of the solid from toluene yielded (45%) pure crystalline **4b**: mp 126°C; IR (KBr) 3362vs, 1561vs, 1527vs, 1510vs, 1456s, 1413vs, 1395vs, 1362s, 1135s, 1027vs, 1007vs, 950vs, 810s, 633m, 600m cm^{-1}; ^1H NMR (acetone-d_6) δ 4.86 (t, J = 7.5 Hz, 2H, OH), 5.30 (d, J = 6.5 Hz, 4H, CH_2), 8.36 (d, J = 2.3 Hz, 1H, ar-H), 8.74 (d, J = 2.3 Hz, 1H, ar-H); ^1H NMR (CD_3CN) δ 4.00 (t, J = 7.3 Hz, 2H, OH), 5.20 (d, J = 6.1 Hz, 4H, CH_2), 8.32 (d, J = 2.3 Hz, 1H, ar-H), 8.71 (d, J = 2.3 Hz, 1H, ar-H); MS m/z 156(M^+, 1), 126 (15), 109(10), 108(22), 96(51), 80(31), 68(29), 54(99), 53(100), 43(23), 42(56), 41(46). Anal. Calcd for $C_5H_8N_4O_2$: C, 38.46; H, 5.16; N, 35.88. Found: C, 38.43; H, 5.15; N, 35.87.

Reaction of 5-nitro-2-aminopyrimidine (1c) and PF. The amine **1c** (1.00 g, 7.1 mmol) and PF (0.23 g, 7.8 mmol) in toluene (20 mL) were refluxed during 5 h to obtain a clear yellow solution. Evaporation of the solvent under reduced pressure gave a solid, which contained three components, namely unreacted amine **1c** (38%), its N-hydroxymethyl derivative **3c** (50%) and its N,N-dihydroxymethyl derivative **4c** (12%), as determined on the basis of the ^1H NMR spectrum of the intact mixture. Attempts to separate the components by crystallization from several different solvents failed to yield any pure substance. ^1H NMR (CD_3CN, on a reaction mixture) for **3c**: δ 3.00 (t, J = 7.3 Hz, 1H, OH), 4.92 (overlapping dd showing as a pseudo t, J = 7.1 Hz, 2H, CH_2), 7.48 (broad s, 1H, NH), 9.06, 9.12 (AB spin system, J = 3.3 Hz, 2H, ar-H); ^1H NMR (CD_3CN, on a reaction mixture) for **4c**: δ 4.17 (t, J = 7.7 Hz, 2H, OH), 5.21 (d, J = 7.5 Hz, 4H, CH_2), 9.16 (s, 2H, ar-H).

Reaction of the mixture obtained from 5-nitro-2-aminopyrimidine (3c) and PF with TMSC. A solution of the title mixture (39.1 mg) and TMSC (0.1 mL, 0.8 mmol) in pyridine (0.2 mL) was kept at 70°C during 30 min. The solution was then analyzed by GC-MS, after distilling off excess TMSC. A mixture of four compounds, namely, 2-amino-5-nitropyrimidine [**1c**, 29%; MS m/z 140(M^+, 100), 124(3), 110(10), 82(9), 80(12), 67(41), 52(26)], its N-trimethylsilyl derivative [**13**, 4%; MS m/z 212(M^+, 29), 197(100), 167(12), 166(10), 151(63), 100(12), 99(10), 73(16)], the O-trimethylsilyl derivative [**14**, 4%; MS m/z 242(M^+, 5), 227(16), 197(8), 125(10), 75(100), 73(24)] of **3c** and the N,N-bis-(O-trimethylsilyl) derivative [**15**, 63%; MS:

344(M^+, 0.2), 329(6), 313(1), 239(4), 254(22), 241(59), 147(62), 103(28), 75(37), 73(100)] of **4c**, was obtained in the ratios shown in brackets: the components were identified from their MS pattern.

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