Bathochromic 1-Amino-2(1*H*)-pyrimidinimines and Hydrazones by Substitution/Dimroth Rearrangement of 1-Amino-2-methylthiopyrimidinium Salts

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1-Amino-2-methylthiopyrimidinium salts **1** and **9** react with hydrazines **2** or alkylamines **6** by substitution of the methylthio group and Dimroth rearrangement affording violet or purple 2(1*H*)-pyrimidinehydrazones **5** and **7** or orange hydrazones **8**, rather than the non-rearranged hydrazones **10** or zwitterionic 1-amido-2-hydrazinopyrimidinium ylides **4** as previously reported.

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Recently we reported on the reaction of 1-amino-2-methylthiopyrimidinium salts **1** with hydrazine **2** (R^2 = H), leading to substitution of the methylthio group. The unusual color (violet or purple) of the products, combined with further chemical transformations, led us to the interpretation that zwitterionic 1-amido-2-hydrazinopyrimidinium-*N*-ylides **4** were obtained rather than the commonly expected 1-amino-2(1*H*)-pyrimidinehydrazones **3** [1]. Since no X-ray crystal analysis was possible, the final proof for the zwitterionic structures **4** is still missing. In order to obtain further evidence for this unusual phenomenon, we tried to synthesize structural analogues of **3** or **4**. 1-Amido-2-aminothiopyrimidinium-*N*-ylides **11** could by synthesized by electrophilic amination of 1-amino-2(1*H*)-pyrimidinethiones and unambiguously confirmed by X-ray structural analysis [2]. Unlike the violet or purple compounds considered as *N*-ylides **4** [1], these *S*-analoguos 2-aminothio-1-amidopyrimidinium-*N*-ylides **11** exhibit a light yellow color.

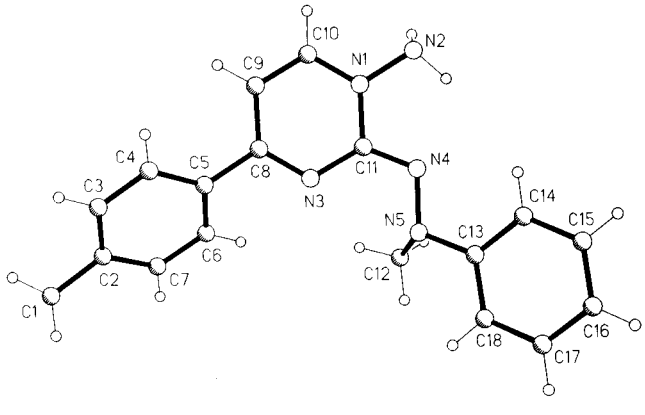


Figure 1. X-Ray Structural Analysis of **8a**.

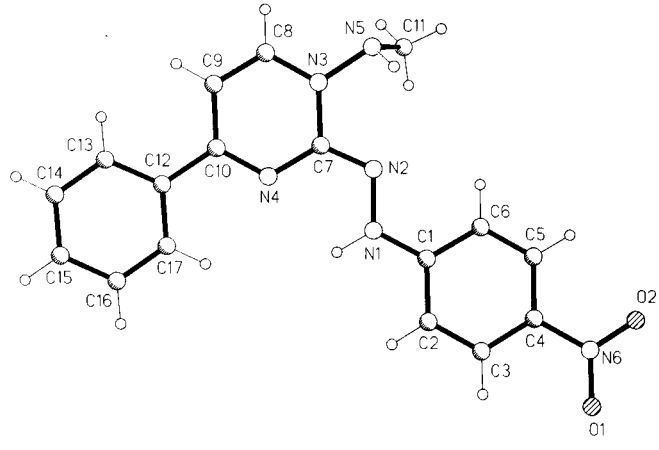
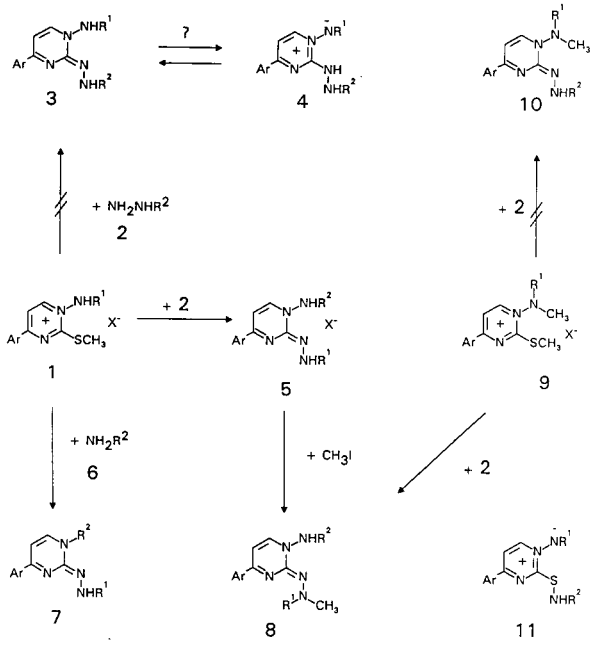


Figure 2. X-Ray Structural Analysis of **5d**.

We now report further investigations of the reactions of 1-amino-2-methylthiopyrimidinium salts **1** and **9** with hydrazines or primary aliphatic amines, leading to the conclusion that the originally published 1-amido-2-hydrazinopyrimidinium-*N*-ylide structure **4** and its assumed methylation product **10** as well as other derivatives have to be revised.

The reported product **10a** (Ar = 4-$CH_3C_6H_4$, R^1 = C_6H_5, R^2 = H, obtained either by methylation of a presumed *N*-ylide **4** (Ar = 4-$CH_3C_6H_4$, R^1 = C_6H_5, R^2 = H) or by condensation of an appropriate 1-amino-2-methylthiopyrimidinium salt **9** (Ar = 4-$CH_3C_6H_4$, R^1 = C_6H_5) with hydrazine **2** (R^2 = H) was investigated by X-ray crystal analysis (see Figure 1). The results clearly demonstrate that the originally assigned structure **10** is wrong. Instead a rearranged 1-amino-2(1*H*)-pyrimidinehydrazone **8a** (R^1 = C_6H_5, R^2 = H) exists. Reactions of the 1-amino-2-methylthiopyrimidinium salts **1** (R^1 = aryl) with methylhydrazine **2** (R^2 = CH_3) give products that have very similar spectroscopic data and colors to the previously reported

compounds assigned to **4** (R^2 = H) [1]. For example, the solution of the 1-phenylamino (R^1 = C_6H_5, R^2 = CH_3) or 1-(4-nitrophenylamino) (R^1 = 4-$NO_2C_6H_4$, R^2 = CH_3) substituted compounds are violet or purple respectively. One of the purple compounds obtained from the reaction of the 1-(4-nitrophenylamino) substituted 2-methylthiopyrimidinium salt **1** (R^1 = 4-$NO_2C_6H_4$, Ar = C_6H_5) and methylhydrazine **2** (R^2 = CH_3), was suitable for X-ray crystal structure determination. The result reveals (see Figure 2) that neither a 1-(4-nitrophenylamido)-2-methylhydrazino-*N*-ylide-structure **4** nor a 1-(4-nitrophenylamino)-2(1*H*)-pyrimidinemethylhydrazone **3** was formed, but the 1-methylamino-2(1*H*)-pyrimidine-(4-nitrophenyl)hydrazone **5d**. Obviously, in addition to the displacement of the methylthio group, a Dimroth rearrangement occurred, moving the original hydrazine moiety R^1NHN from an endocyclic to an exocyclic position. Since all other products obtained with methylhydrazine as well as with hydrazine (see ref [1] and further examples in the experimental part of this paper) exhibit similar uv, ^1H and ^{13}C nmr data, they must belong to the same series of rearranged 1-amino-2(1*H*)-pyrimidinehydrazones **5**, including the compounds previously assigned as **4** [1]. Furthermore the new reaction of 1-amino-2-methylthiopyrimidinium salts **1** with primary alkylamines **6** also results in corresponding rearranged products **7** exhibiting unusual purple or violet colors. All structures **5** and **7** are characterized by a typical signal between 92 and 96.4 ppm in the ^{13}C nmr, which was previously erroneously assigned to a C4 carbon atom of a phenylamido substituent in the incorrect ylide structure **4** (R^1 = C_6H_5). Instead this signal belongs to the carbon atom at position 5 of the pyrimidine ring [3].



	R^1	R^2	Ar
5a	C_6H_5	H	4-ClC$_6H_4$
5b	C_6H_5	CH_3	4-$CH_3C_6H_4$
5c	4-$NO_2C_6H_4$	H	4-$CH_3C_6H_4$
5d	4-$NO_2C_6H_4$	CH_3	C_6H_5
5e	4-$NO_2C_6H_4$	CH_3	4-$CH_3C_6H_4$
5f	2,4-$(NO_2)_2C_6H_3$	CH_3	C_6H_5
5g	2,4-$(NO_2)_2C_6H_3$	CH_3	4-$CH_3C_6H_4$
5h	4-$CH_3C_6H_4SO_2$	H	C_6H_5
5i	C_6H_5CO	H	4-$CH_3OC_6H_4$
7a	4-$NO_2C_6H_4$	CH_3CH_2	C_6H_5
7b	4-$NO_2C_6H_4$	$CH_3(CH_2)_2$	C_6H_5
7c	2,4-$(NO_2)_2C_6H_3$	$CH_3(CH_2)_2$	C_6H_5
8a	C_6H_5	H	4-$CH_3C_6H_4$

The color of the compounds **5** and **7** seems to be independent of the substituent R^2 in position 1, but it does depend on R^1. It ranges from violet (R^1 = C_6H_5) *via* purple (R^1 = 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$, 4-$CH_3C_6H_4SO_2$) to deep red (R^1 = benzoyl). These colors are quite exceptional for 2(1*H*)-pyrimidinehydrazone structures, which are usually yellow or orange [4,5]. We have no explanation yet for this phenomenon, or for the strong negative solvatochromism [1]. But the hydrogen atom at the hydrazone nitrogen atom of **5** seems to be essential for the deep color as implied by, for example, the comparison of the violet compound **5b** (R^1 = C_6H_5, R^2 = H, Ar = 4-$CH_3C_6H_4$) [1] with the corresponding orange *N*-methyl derivatives **8a**.

The structures of further derivatives (3-amino-1,3,4-triazolo[3,2-*a*]pyrimidinium salts, pyrimido[1,2-*b*]benzo-1,2,4-triazinium dibromide) given in the previous publication [1] also have to be revised on the basis of the correct structure **5**.

Table 1

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (pm^2 x 10^{-1}) for Compound 5d

	x	y	z	U(eq)
N(1)	5776(2)	4217.1(11)	5946(2)	34.9(11)
N(2)	6048(2)	4916.1(12)	6781(2)	35.3(11)
N(3)	7266(2)	6173.9(12)	7299(2)	35.4(11)
N(4)	7643(2)	5374.4(11)	5427(2)	32.1(10)
N(5)	6522(2)	6327.2(14)	8344(2)	44.5(12)
N(6)	1947(2)	1725.1(13)	6946(2)	42.0(11)
O(1)	1531(2)	1196.8(12)	6096(2)	56.9(11)
O(2)	1488(2)	1728.4(12)	7989(2)	54.7(11)
C(1)	4871(2)	3600.8(13)	6210(2)	29.7(11)
C(2)	4532(2)	2895.3(14)	5353(2)	31.9(12)
C(3)	3585(2)	2291.8(14)	5593(2)	32.6(12)
C(4)	2968(2)	2344.4(14)	6712(2)	32.7(12)
C(5)	3311(2)	3018.8(15)	7578(2)	36.0(12)
C(6)	4245(2)	3641.0(15)	7336(2)	34.4(13)
C(7)	6974(2)	5452.6(14)	6481(2)	31.7(12)
C(8)	8234(2)	6756(2)	7083(2)	38.6(13)
C(9)	8920(2)	6666.4(15)	6069(2)	38.4(13)
C(10)	8575(2)	5953.5(14)	5213(2)	31.4(11)
C(11)	6911(3)	5715(2)	9381(2)	59(2)
C(12)	9219(2)	5841.3(14)	4037(2)	32.9(12)
C(13)	10200(2)	6421(2)	3694(2)	43.1(14)
C(14)	10744(3)	6316(2)	2572(2)	50(2)
C(15)	10344(3)	5628(2)	1767(2)	47(2)
C(16)	9380(2)	5047(2)	2092(2)	43.9(15)
C(17)	8823(2)	5148.2(15)	3212(2)	38.8(13)

Table 2

Selected Bond Lengths (pm) and Angles (°) for Compound **5d**

N(1)-C(1)	134.7(3)	N(1)-N(2)	138.3(2)
N(2)-C(7)	129.6(3)	N(3)-C(8)	134.6(3)
N(3)-C(7)	140.1(3)	N(3)-N(5)	142.1(3)
N(4)-C(10)	131.6(3)	N(4)-C(7)	137.0(3)
N(5)-C(11)	145.9(3)	N(6)-O(1)	124.4(2)
N(6)-O(2)	124.5(2)	N(6)-C(4)	142.6(3)
C(1)-C(6)	141.0(3)	C(1)-C(2)	141.6(3)
C(2)-C(3)	135.8(3)	C(3)-C(4)	140.1(3)
C(4)-C(5)	138.8(3)	C(5)-C(6)	136.8(3)
C(8)-C(9)	134.6(3)	C(9)-C(10)	142.4(3)
C(10)-C(12)	147.6(3)		
C(1)-N(1)-N(2)	118.7(2)	C(7)-N(2)-N(1)	114.4(2)
C(8)-N(3)-C(7)	120.3(2)	C(8)-N(3)-N(5)	118.6(2)
C(7)-N(3)-N(5)	121.1(2)	C(10)-N(4)-C(7)	120.3(2)
N(3)-N(5)-C(11)	111.6(2)	O(1)-N(6)-O(2)	121.5(2)
O(1)-N(6)-C(4)	119.0(2)	O(2)-N(6)-C(4)	119.5(2)
N(1)-C(1)-C(6)	121.2(2)	N(1)-C(1)-C(2)	120.1(2)
C(6)-C(1)-C(2)	118.7(2)	C(3)-C(2)-C(1)	120.3(2)
C(2)-C(3)-C(4)	120.2(2)	C(5)-C(4)-C(3)	120.3(2)
C(5)-C(4)-N(6)	119.6(2)	C(3)-C(4)-N(6)	120.1(2)
C(6)-C(5)-C(4)	120.1(2)	C(5)-C(6)-C(1)	120.4(2)
N(2)-C(7)-N(4)	125.1(2)	N(2)-C(7)-N(3)	115.9(2)
N(4)-C(7)-N(3)	119.0(2)	N(3)-C(8)-C(9)	120.8(2)
C(8)-C(9)-C(10)	118.4(2)	N(4)-C(10)-C(9)	121.1(2)
N(4)-C(10)-C(12)	117.0(2)	C(9)-C(10)-C(12)	121.9(2)

Table 3

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (pm^2 x 10^{-1}) for Compound **8a**

	x	y	z	U(eq)
C(1)	609(2)	8161(4)	787(2)	42.6(14)
C(2)	1348(2)	6316(4)	760.9(13)	30.4(12)
C(3)	1461(2)	5148(4)	136.8(12)	31.7(12)
C(4)	2169(2)	3512(4)	110.1(12)	29.6(12)
C(5)	2803(2)	3031(4)	708.9(11)	22.9(11)
C(6)	2678(2)	4178(4)	1340.4(11)	25.3(11)
C(7)	1959(2)	5770(4)	1363.5(12)	29.5(13)
C(8)	3584(2)	1337(3)	697.6(11)	21.7(11)
C(9)	3419(2)	-644(4)	307.1(11)	27.0(12)
C(10)	4134(2)	-2216(4)	367.2(11)	24.4(12)
C(11)	5146(2)	177(3)	1137.9(10)	20.4(11)
C(12)	5707(2)	-2804(4)	2447.9(12)	30.1(12)
C(13)	7209(2)	2997(3)	1852.7(11)	23.0(11)
C(14)	7916(2)	1580(4)	1611.9(12)	28.4(13)
C(15)	8900(2)	2194(4)	1677.5(13)	37.0(13)
C(16)	9201(2)	4201(4)	1972.3(14)	37.8(13)
C(17)	8505(2)	5618(4)	2197.4(14)	38.8(14)
C(18)	7520(2)	5059(4)	2137.8(13)	33.3(13)
N(1)	4955.1(13)	-1865(3)	791.1(9)	22.7(10)
N(2)	5692(2)	-3522(3)	832.4(11)	29.5(12)
N(3)	4421.0(13)	1753(3)	1086.6(9)	21.6(9)
N(4)	6007.6(13)	327(3)	1485.9(9)	22.1(10)
N(5)	6196.6(13)	2483(3)	1791.6(9)	23.5(10)

The results reported above demonstrate that the Dimroth rearrangement found in substitution reactions of the 2-methylthio group in 1-aryl-2-methylthiopyrimidinium salts with hydrazines [6] also occurs in corresponding reactions of 1-arylamino or 1-acylamino-2-methylthiopyrimidinium salts **1** or **9** with hydrazines. A reasonable mechanism was proposed in the previous publication [6].

Table 4

Selected Bond Lengths (pm) and Angles (°) for Compound **8a**

C(5)-C(8)	147.8(3)	C(8)-N(3)	132.8(3)
C(8)-C(9)	140.8(3)	C(9)-C(10)	135.8(3)
C(10)-N(1)	133.7(3)	C(11)-N(4)	130.1(3)
C(11)-N(3)	136.9(3)	C(11)-N(1)	140.5(3)
C(12)-N(5)	146.7(3)	C(13)-N(5)	141.4(3)
N(1)-N(2)	141.5(3)	N(4)-N(5)	143.4(2)
N(3)-C(8)-C(9)	122.6(2)	N(3)-C(8)-C(5)	116.8(2)
C(9)-C(8)-C(5)	120.5(2)	C(10)-C(9)-C(8)	117.7(2)
N(1)-C(10)-C(9)	120.1(2)	N(4)-C(11)-N(3)	127.3(2)
N(4)-C(11)-N(1)	114.7(2)	N(3)-C(11)-N(1)	118.0(2)
C(10)-N(1)-C(11)	121.8(2)	C(10)-N(1)-N(2)	118.7(2)
C(11)-N(1)-N(2)	119.2(2)	C(8)-N(3)-C(11)	119.5(2)
C(11)-N(4)-N(5)	112.9(2)	C(13)-N(5)-N(4)	111.8(2)
C(13)-N(5)-C(12)	114.7(2)	N(4)-N(5)-C(12)	112.1(2)

EXPERIMENTAL

Melting points were determined on a Boetius heating block. The ir spectra were measured on a Specord IR 72 Carl-Zeiss Jena. The nmr spectra were obtained either on a Bruker 300 MHz or a BS 487C 80 MHz Tesla Brno. The mass spectra were obtained with a HP 5995 A, Hewlett Packard, 70 eV. The uv-visible spectra were determined with a Specord, Carl-Zeiss Jena. Compound **8a** was prepared following the reported procedure for the erroneously assigned product **10a** (numbered **8a** in the original paper [1]). Known compounds **5** (**5a**, **5c**, **5i**) previously considered as *N*-ylides **4** (numbered as **5h**, **5d**, and **5j** respectively in the original publication [1]) stem from the same source.

1-Amino-1,2-dihydropyrimidine-2-imines **5** and 1-Amino-2(1*H*)-pyrimidinehydrazones **7** and **8**.

A mixture of 1-amino-2-methylthiopyrimidinium iodide **1** (X = I) (0.01 mole), or **9**, ethanol (20 ml) and hydrazine **2** (0.015 mole) or amine **6** is stirred for 10 minutes and then shortly heated to boiling. After cooling to room temperature the product is filtered by suction and recrystallized.

4-(4-Chlorophenyl)-2-(phenylhydrazono)-2*H*-pyrimidin-1-ylamine (**5a**) [1].

This compound was obtained according to reference [1]; ^{13}C nmr (dimethyl sulfoxide-d_6): 92.34 (*C*H=CHN), 111.81 (CH phenyl), 116.07 (CH phenyl), 128.50 (CH phenyl), 128.55 (CH phenyl), 129.36 (C quart), 134.72 (C quart), 136.16 (CH phenyl), 143.65 (C quart), 147.18 (CH=*C*HN), 148.54 (C quart), 162.42 (C quart); ms: m/z 311 (M^+, 4), 191 (13), 105 (20), 93 (19), 77 (100); uv (dichloromethane): λ max 293 (4.45), 521 nm (log ε 3.83), violet solution.

Methyl-[2-(phenylhydrazono)-4-(4-tolyl)-2*H*-pyrimidin-1-yl]amine (**5b**).

This compound was obtained as black crystals (ethanol), mp 195-197°, yield 71%; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.37 (s,

3H, CH_3), 3.38 (s, 3H, CH_3NH), 6.21 (d, 1H, J = 7.3 Hz, CH = CH), 6.65 (m, 3H, C_6H_5, NH), 7.22 (m, 5H, C_6H_5, C_6H_4), 7.40 (m, 2H, C_6H_4), 7.80 (d, 1H, J = 7.3 Hz, CH = CH); ^{13}C nmr (pyridine-d_5): δ 21.20 ($CH_3C_6H_4$), 59.00 (CH_3NH), 96.40 (*C*H = CHN), 114.60 (CH phenyl), 119.60 (CH phenyl), 127.50 (CH phenyl), 129.40 (CH phenyl), 129.60 (CH phenyl), 134.40 (C quart), 141.40 (CH phenyl), 143.40 (C quart), 146.70 (CH = *C*H-N), 147.70 (C quart), 163.30 (C quart); ms: m/z 305 (M^+, 5), 171 (34), 117 (23), 115 (28), 91 (24), 77 (100), 65 (41), 51 (37), 39 (32), 28 (31); uv (chloroform): λ max 320 (4.35), 513 nm (log ε 2.60), violet solution.

Anal. Calcd. for $C_{18}H_{19}N_5$ (305.39): C, 70.79; H, 6.28; N, 22.94. Found: C, 70.99; H, 6.39; N, 22.72.

2-[(4-Nitrophenyl)hydrazono]-4-(4-tolyl)-2*H*-pyrimidin-1-ylamine (**5c**) [1].

This compound was obtained according to reference [1]; ^{13}C nmr (dimethyl sulfoxide-d_6): δ 21.06 (CH_3), 94.78 (*C*H = CHN), 110.2 (CH phenyl), 126.04 (CH phenyl), 127.91 (CH phenyl), 129.20 (CH phenyl), 132.71 (C quart), 134.75 (C quart), 141.84 (C quart), 147.03 (C quart), 148.26 (CH = *C*H-N), 150.58 (C quart), 163.96 (C quart); uv (dichloromethane): λ max = 293 (4.14), 461 nm (log ε 4.44), purple solution.

Anal. Calcd. for $C_{17}H_{16}N_6O_2$ (336.36): C, 60.70; H, 4.79; N, 24.99. Found: C, 60.45; H, 4.98; N, 25.10.

Methyl-{2-[(4-nitrophenyl)hydrazono]-4-phenyl-2*H*-pyrimidin-1-yl}amine (**5d**).

This compound was obtained as dark-green crystals (ethanol), mp 178-179°, yield 97%; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.48 (s, 3H, CH_3), 6.06 (m, 1H, NH), 6.47 (d, 1H, J = 7.1 Hz, CH = CH), 7.55 (m, 3H, C_6H_5), 7.60 (m, 4H, C_6H_4, C_6H_5), 7.85 (d, 1H, J = 7.1 Hz, CH = CH), 8.15 (m, 2H, C_6H_4), 9.55 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 36.44 (CH_3), 95.65 (*C*H = CHN), 110.20 (CH phenyl), 126.06 (CH phenyl), 127.98 (CH phenyl), 128.59 (CH phenyl), 131.83 (C quart), 134.99 (C quart), 135.33 (CH phenyl), 144.99 (C quart), 148.90 (CH = *C*H-N), 150.69 (C quart), 164.65 (C quart); ms: m/z 336 (M^+, 91), 307 (48), 306 (100), 232 (22), 231 (22), 170 (19), 157 (79), 156 (70), 155 (58), 129 (66); uv (acetonitrile): λ max 218.5 (4.24), 280 (4.37), 468 nm (log ε 4.41), purple solution.

Anal. Calcd. for $C_{17}H_{16}N_6O_2$ (336.36): C, 60.70; H, 4.80; N, 24.99. Found: C, 61.03; H, 4.92; N, 24.94.

Methyl-{2-[(4-nitrophenyl)hydrazono]-4-(4-tolyl)-2*H*-pyrimidin-1-yl}amine (**5e**).

This compound was obtained as black crystals (ethanol), mp 145-147°, yield 89%; ^1H nmr (deuteriochloroform): δ 2.50 (s, 3H, CH_3), 3.10 (s, 3H, CH_3NH), 5.40 (br, 1H, NH), 6.88 (d, 1H, J = 7.3 Hz, CH = CH), 7.30 (m, 4H, C_6H_4), 7.67 (m, 4H, C_6H_4), 8.35 (d, 1H, J = 7.3 Hz, CH = CH), 9.10 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 21.23 ($CH_3C_6H_4$), 56.27 (CH_3NH), 95.77 (*C*H = CHN), 110.38 (CH phenyl), 126.18 (CH phenyl), 128.16 (CH phenyl), 129.39 (CH phenyl), 132.88 (C quart), 135.30 (C quart), 135.4 (C quart), 145.24 (C quart), 148.64 (CH = *C*H-N), 150.88 (C quart), 164.77 (C quart); ms: m/z 350 (M^+, 36), 321 (44), 320 (53), 185 (23), 184 (41), 171 (69), 170 (62), 169 (100), 155 (40), 143 (34), 142 (25), 128 (27), 122 (72), 118 (29), 117 (35), 116 (45), 115 (83), 92 (27), 91 (54), 76 (44), 75 (35), 65 (36), 64 (23), 63 (29), 30 (40), 28 (29); uv (chloroform): λ max 299 (4.40), 467 nm (log ε 4.26), purple solution.

Anal. Calcd. for $C_{18}H_{18}N_6O_2$ (350.39): C, 61.70; H, 5.19; N, 23.99. Found: C, 61.64; H, 5.20; N, 24.25.

Methyl-{2-[(2,4-dinitrophenyl)hydrazono]-4-phenyl-2*H*-pyrimidin-1-yl}amine (**5f**).

This compound was obtained as black crystals (acetic acid), mp 266-267°, yield 89%; ms: m/z 381 (M^+, 64), 351 (55), 157 (28), 156 (54), 155 (100), 129 (79), 128 (33), 115 (38), 104 (33), 103 (65), 102 (48), 91 (15), 77 (63), 75 (41), 30 (46); uv (DMF): λ max 452 nm (log ε 4.32), red-brown solution.

Anal. Calcd. for $C_{17}H_{15}N_7O_4$ (381.36): C, 53.54; H, 3.97; N, 25.72. Found: C, 53.23; H, 4.11; N, 25.41.

Methyl-{2-[(2,4-dinitrophenyl)hydrazono]-4-(4-tolyl)-2*H*-pyrimidin-1-yl}amine (**5g**).

This compound was obtained as black crystals (acetic acid), mp 271-273°, yield 93%; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.33 (s, 3H, $CH_3C_6H_4$), 3.40 (s, 3H, CH_3NH), 6.91 (d, 1H, J = 7.0 Hz, CH = CH), 7.50 (m, 2H, C_6H_4), 8.20 (m, 5H, C_6H_3, C_6H_4), 8.29 (d, 1H, J = 7.0 Hz, CH = CH), 12.51 (s, 1H, NH); ms: m/z 395 (M^+, 61), 365 (51), 171 (28), 170 (51), 169 (100), 143 (33), 142 (28), 129 (30), 128 (33), 118 (31), 117 (50), 115 (97), 91 (88), 77 (30), 76 (20), 65 (35), 63 (45), 39 (34), 38 (24); uv (DMF): λ max 280 (4.41), 305 (4.43), 449 nm (log ε 4.40), red-brown solution.

Anal. Calcd. for $C_{18}H_{17}N_7O_4$ (395.39): C, 54.68; H, 4.34; N, 24.80. Found: C, 54.20; H, 4.56; N, 24.83.

2-[(4-Tolylsulfonyl)hydrazono]-4-phenyl-2*H*-pyrimidin-1-ylamine (**5h**).

This compound was obtained as purple crystals (ethanol), mp 181-183°, yield 80%; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.45 (s, 3H, CH_3), 5.73 (m, 2H, NH_2), 6.41 (m, 2H, C_6H_4), 7.35 (d, 1H, J = 7.0 Hz, CH = CH), 7.52 (m, 3H, C_6H_5), 7.79 (m, 2H, C_6H_4), 7.87 (d, 1H, J = 7.0 Hz, CH = CH), 8.15 (m, 2H, C_6H_5), 9.02 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 20.94 (CH_3), 94.98 (*C*H = CHN), 127.63 (CH phenyl), 127.70 (CH phenyl), 128.56 (CH phenyl), 129.06 (CH phenyl), 131.57 (C quart), 135.53 (C quart), 136.16 (CH phenyl), 142.49 (CH phenyl), 147.61 (C quart), 148.70 (CH = *C*H-N), 163.91 (C quart); ms: m/z 355 (M^+, 6), 200 (89), 185 (37), 172 (76), 157 (47), 156 (57), 155 (43), 129 (40), 104 (100), 103 (46), 102 (31), 92 (30), 91 (82), 77 (68), 69 (46), 51 (43), 44 (46), 28 (40), 18 (58); uv (chloroform): λ max 279 (4.53), 436 nm (log ε 3.11), red solution.

Anal. Calcd. for $C_{17}H_{17}N_5O_2S$ (355.43): C, 57.44; H, 4.83; N, 19.71. Found: C, 57.74; H, 4.98; N, 19.99.

2-Benzoylhydrazono-4-(4-methoxyphenyl)-2*H*-pyrimidin-1-ylamine (**5i**) [1].

This compound was obtained according to reference [1]; ^{13}C nmr (dimethyl sulfoxide-d_6): δ 55.43 (CH_3), 95.04 (*C*H = CHN), 114.22 (CH phenyl), 126.62 (CH phenyl), 127.87 (CH phenyl), 128.62 (C quart), 129.38 (CH phenyl), 130.72 (CH phenyl), 134.94 (C quart), 148.14 (CH = *C*HN), 149.68 (C quart), 160.21 (C quart), 162.26 (C quart), 163.55 (C quart); ms: m/z 335 (M^+, 36), 320 (24), 218 (18), 202 (26), 187 (19), 134 (36), 105 (100), 77 (59); uv (DMF): λ max 319 (4.53), 451 nm (log ε 3.17), red solution.

Anal. Calcd. for $C_{18}H_{17}N_5O_2$ (335.37): C, 64.46; H, 5.11; N, 20.89. Found: C, 63.34; H, 5.21; N, 20.73.

N-(1-Ethyl-4-phenyl-1*H*-pyrimidin-2-ylidene)-*N'*-(4-nitrophenyl)hydrazine (**7a**).

This compound was obtained as dark-green crystals (ethanol), mp 157-159°, yield 85%; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.37 (t, 3H, J = 7 Hz, CH_3), 3.88 (q, 2H, J = 7 Hz, CH_2), 6.54 (d, 1H, J =

6.9 Hz, CH=CH), 7.95 (m, 3H, C_6H_5), 7.99 (d, 1H, J = 6.9 Hz, CH=CH), 8.25-8.35 (m, 6H, C_6H_4, C_6H_5), 9.87 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 12.48 (CH_3), 45.86 (CH_2), 96.10 (*C*H=CHN), 110.06 (CH phenyl), 126.15 (CH phenyl), 128.58 (CH phenyl), 131.84 (CH phenyl), 134.79 (C quart), 135.44 (C quart), 146.02 (C quart), 149.20 (CH=*C*H-N), 150.39 (CH phenyl), 150.51 (C quart), 165.37 (C quart); ms: m/z 335 (M^+, 35), 198 (60), 171 (67), 170 (58), 157 (100), 156 (45), 155 (37), 129 (63), 128 (30), 122 (28), 105 (31), 104 (33), 103 (61), 102 (47), 77 (64), 75 (40), 63 (31), 52 (27), 51 (38), 50 (42), 30 (44), 29 (93), 28 (80); uv (chloroform): λ max 313 (4.33), 467 nm (log ε 4.00), purple solution.

Anal. Calcd. for $C_{18}H_{17}N_5O_2$ (335.37): C, 64.46; H, 5.12; N, 20.89. Found: C, 64.24; H, 5.26; N, 20.49.

N-(4-Nitrophenyl)-*N'*-(4-phenyl-1-propyl-1*H*-pyrimidin-2-ylidene)-hydrazine (**7b**).

This compound was obtained as red-violet crystals (ethanol), mp 170-172°, yield 87%; ^{1}H nmr (deuteriochloroform): δ 1.04 (t, 3H, J = 7.3 Hz, CH_3), 2.69 (m, 2H, CH_2), 3.77 (t, 2H, J = 7 Hz, CH_2), 6.14 (d, 1H, J = 6.9 Hz, CH=CH), 7.29 (m, 2H, C_6H_4), 7.55 (d, 1H, J = 6.9 Hz, CH=CH), 7.63 (m, 3H, C_6H_5), 7.91 (m, 2H, C_6H_4), 8.04 (m, 2H, C_6H_5), 8.16 (s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 11.22 (CH_3), 20.10 (CH_3-CH_2), 53.35 (CH_2-CH_2-N), 96.04 (*C*H=CHN), 109.82 (CH phenyl), 126.70 (CH phenyl), 127.23 (CH phenyl), 128.79 (CH phenyl), 131.90 (CH phenyl), 136.00 (C quart), 136.67 (C quart), 145.75 (C quart), 147.76 (CH=*C*HN), 150.15 (C quart), 166.32 (C quart); ms: m/z 349 (M^+, 26), 202 (28), 171 (33), 170 (31), 157 (69), 156 (54), 155 (49), 129 (60), 128 (27), 115 (28), 104 (31), 103 (58), 102 (45), 77 (60), 65 (38), 63 (34), 52 (33), 51 (45), 50 (43), 43 (59), 41 (100), 39 (53), 28 (46); uv (chloroform): λ max 279 (4.25), 316 (4.34), 464 nm (log ε 3.85), purple solution.

Anal. Calcd. for $C_{19}H_{19}N_5O_2$ (349.40): C, 65.31; H, 5.49; N, 20.05. Found: C, 65.05; H, 5.43; N, 20.05.

N-(2,4-Dinitrophenyl)-*N'*-(4-phenyl-1-propyl-1*H*-pyrimidin-2-ylidene)hydrazine (**7c**).

This compound was obtained as black crystals (acetonitrile), mp 288-289°, yield 91%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.00 (t, 3H, J = 7.2 Hz, CH_3), 1.78 (m, 2H, CH_2), 3.69 (t, 2H, J = 6.8 Hz, CH_2), 5.40 (d, 1H, J = 7.0 Hz, CH=CH), 7.60 (m, 3H, C_6H_3), 7.85 (d, 1H, J = 7.0 Hz, CH=CH), 8.60 (m, 5H, C_6H_5); ms: m/z 394 (M^+, 100), 202 (49), 201 (49), 156 (49), 155 (64), 129 (57), 103 (43), 102 (37), 77 (58), 76 (25), 75 (47), 74 (28), 41 (47), 30 (95), 27 (36); uv (chloroform): λ max 274 (4.51), 444 nm (log ε 4.44), red-black solution.

Anal. Calcd. for $C_{19}H_{18}N_6O_4$ (394.40): C, 57.86; H, 4.61; N, 21.31. Found: C, 57.90; H, 4.59; N, 21.45.

X-Ray Structure Determination of Compound **5d**.

Compound **5d** ($C_{17}H_{16}N_6O_2$, M = 336.4) crystallized from ethanol as monoclinic crystals in the space group $P2_1/n$ with a = 1010.2(2), b = 1495.9(3), c = 1065.1(2) pm, β = 95.58(2)°, U = 1.6019(5) nm^3, Z = 4, D_x = 1.395 Mg m^{-3}, λ(MoKα) = 71.073 pm, μ = 0.1 mm^{-1}, F(000) = 704, T = 143K. Data collection and reduction: A purple tablet 0.5 x 0.4 x 0.2 mm was used to collect 5610 intensities on a Siemens R3 diffractometer ($2\theta_{max}$ 50°, 2826 unique, R_{int} 0.034). The orientation matrix was refined from setting angles of 50 reflections in the 2θ range 20-23°. Structure solution and refinement: The structure was solved by direct methods and refined anisotropically on F^2. H atoms were included using a riding model. The final wR (F^2) for all reflections and 230 parameters was 0.143, with a conventional R (F) 0.048. Final atomic coordinates are given in Table 1, with selected bond lengths and angles in Table 2.

X-Ray Structure Determination of Compound **8a**.

Compound **8a** ($C_{18}H_{19}N_5$, M = 305.4) was obtained as reported before ([1] assigned as **10**) by reaction of the corresponding 1-(*N*-methylanilino)-2-methylthiopyrimidinium iodide **9** with hydrazine hydrate. The compound formed monoclinic crystals from ethanol in the space group $P2_1/c$ with a = 1367.7(2), b = 601.78(10), c = 1880.3(3) pm, β = 94.94(2)°, U = 1.5418(4) nm^3, Z = 4, D_x = 1.316 Mg m^{-3}, λ(MoKα) = 71.073 pm, μ = 0.08 mm^{-1}, F(000) = 648, T = 143K. Data collection and reduction: A red-brown plate 0.65 x 0.45 x 0.08 mm was used to collect 3829 intensities on a Stoe STADI-4 diffractometer ($2\theta_{max}$ 55°, 3532 unique, R_{int} 0.048). The cell constants were refined from ± ω angles of 68 reflections in the 2θ range 20-23°. Structural solution and refinement: As for **5d**, the final wR (F^2) for all reflections and 218 parameters was 0.145, with a conventional R (F) 0.057. Final atomic coordinates are given in Table 3, with selected bond lengths and angles in Table 4.

Crystal Data.

The program SHELXS/SHELXL-92 was employed. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD....400142 (compound **8a**) and 400143 (compound **5d**).

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