Dimroth-Rearranged Products in the Reactions of 1-Aryl-2-methylthiopyrimidinium Salts with Hydrazines

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Reaction of 1-aryl-2-methylthiopyrimidinium salts with hydrazine does not lead to substitution at C-2 but to rearrangement into 1,2-diaminopyrimidinium salts. An ANRORC-mechanism involving an azatriene as intermediate is proposed.

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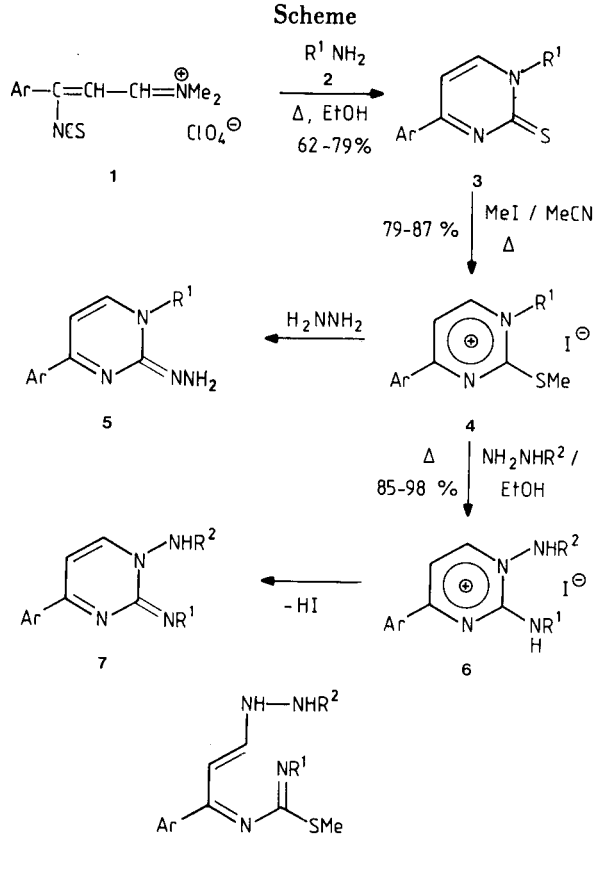
Recently we have found an efficient access to 1-substituted-4-aryl-2-methylthiopyrimidinium salts **4** [1,2] from 3-aryl-3-isothiocyanato-2-propeniminium salts **1**. These salts **1** were reacted with primary amines **2** or hydrazines **2** ($R^1 = R^2NH$) to give 2(1*H*)-pyrimidinethiones **3**, which by treatment with methyl iodide are converted into salts **4** (see also Experimental). A number of hitherto unknown 1-aryl-2(1*H*)-pyrimidinethiones **3** and 1-aryl-2-methylthiopyrimidinium iodides **4** are prepared by this method as shown in Table 1. The methylthio group of pyrimidinium salts **4** can easily be substituted by nucleophiles [3]. Hydrazine, for example, has been reported to react with 1-amino substituted 2-methylthiopyrimidinium salts **4** (R^1 = arylNH, RCONH or phenyl-*N*-methyl) to yield 2(1*H*)-pyrimidinehydrazones **5** or the corresponding tautomeric 1-amino-2-hydrazinopyrimidine-*N*-ylides [4]. The original pyrimidine ring skeleton of **4** is retained in compound **5**. We now report on a rearrangement reaction of 1-aryl-substituted 2-methylthiopyrimidinium iodides **4** (R^1 = aryl) in reaction with hydrazine or phenylhydrazine. The reaction is performed under the same conditions as used in the case of 1-amino-substituted compounds **4** [4], *i.e.* by a short reflux of the reactants in ethanolic solution. Stable crystalline products are obtained in high yields. Structure elucidation revealed that rearrangement into 1-amino-2-arylaminopyrimidinium iodides **6** rather than into the expected substitution products **5** (R^1 = aryl) has taken place. In some cases, **7d** and **7f**, not 1,2-diaminopyrimidinium salts **6** but the corresponding yellow-colored neutral substances 1-amino-2(1*H*)-pyrimidinimines **7** are obtained. This deprotonation reaction probably is caused by the different solubility of the corresponding **6** and **7**. Since by ^{1}H-nmr spectroscopy the distinction between possible structures **5** or **6** could not be unequivocally established we proved the structure of the 1,2-diaminopyrimidinium

Scheme



3	4	6	7	Ar	R^1	R^2
a	**a**	**a**		C_6H_5	4-$CH_3OC_6H_4$	H
b	**b**	**b**		4-$CH_3C_6H_4$	C_6H_5	H
b	**b**	**c**		4-$CH_3C_6H_4$	C_6H_5	C_6H_5
d	**d**	**d**	**d**	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	H
e	**e**	**e**		4-$CH_3C_6H_4$	4-BrC_6H_4	H
f	**f**		**f**	4-$CH_3C_6H_4$	2-NCC_6H_4	H
g	**g**	**g**		4-ClC_6H_4	4-$CH_3OC_6H_4$	H
b	**b**		**h**	4-$CH_3C_6H_4$	C_6H_5	COC_6H_5
d	**d**	**i**		4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	C_6H_5

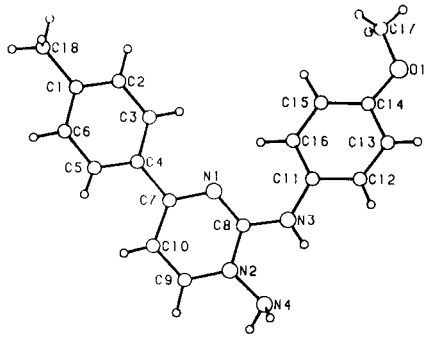


Figure 1. Pluto-drawing of the molecule showing the atomic numbering.

salts by X-ray crystal analysis. We chose for that purpose compound **6d** which is obtained from the free base **7d** by treatment with concentrated hydroiodic acid in acetonitrile.

In the ms of both the pyrimidinium salts **6** and the 2(1*H*)-pyrimidinimines **7** typical fragment peaks are found derived from splitting off the 1-arylamino group. This also demonstrates that 1-amino (R^2 = H) and 1-anilino (R^2 = C_6H_5) substituted compounds **6** belong to the same series of rearranged products. The same is found in the uv-spectra of **6b** and **6c**, which are also very similar. There is a considerable bathochromic shift in the long wave absorption when salts **6** are compared with free bases **7**. Furthermore a considerable difference is found in the chemical shifts of the pyrimidine protons appearing at lower fields for the salts **6**.

Table 1
Bond Distances (Å) and Bond Angles (°) with e.s.d.'s in Parentheses.

C1	-	C2	1.397(5)	C2	-	C1	-	C6	117.9(4)
C1	-	C6	1.388(5)	C2	-	C1	-	C18	121.5(4)
C1	-	C18	1.508(5)	C6	-	C1	-	C18	120.6(4)
C2	-	C3	1.390(4)	C1	-	C2	-	C3	121.8(4)
C3	-	C4	1.405(4)	C2	-	C3	-	C4	119.7(4)
C4	-	C5	1.405(4)	C3	-	C4	-	C5	118.7(3)
C4	-	C7	1.470(4)	C3	-	C4	-	C7	120.7(3)
C5	-	C6	1.383(5)	C5	-	C4	-	C7	120.5(3)
C7	-	C10	1.418(4)	C4	-	C5	-	C6	120.3(4)
C7	-	N1	1.341(4)	C1	-	C6	-	C5	121.7(4)
C8	-	N1	1.328(4)	C4	-	C7	-	C10	121.1(3)
C8	-	N2	1.377(4)	C4	-	C7	-	N1	117.9(3)
C8	-	N3	1.337(4)	C10	-	C7	-	N1	121.1(3)
C9	-	C10	1.352(4)	N1	-	C8	-	N2	122.1(3)
C9	-	N2	1.355(4)	N1	-	C8	-	N3	123.0(3)
C11	-	C12	1.401(4)	N2	-	C8	-	N3	114.8(3)
C11	-	C16	1.382(4)	C10	-	C9	-	N2	120.0(4)
C11	-	N3	1.423(4)	C7	-	C10	-	C9	118.4(4)
C12	-	C13	1.369(4)	C12	-	C11	-	C16	119.4(3)
C13	-	C14	1.388(4)	C12	-	C11	-	N3	116.1(3)
C14	-	C15	1.391(4)	C16	-	C11	-	N3	124.3(3)
C14	-	O1	1.368(4)	C11	-	C12	-	C13	120.4(3)
C15	-	C16	1.389(4)	C12	-	C13	-	C14	120.2(4)
C17	-	O1	1.435(5)	C13	-	C14	-	C15	119.8(3)
N2	-	N4	1.413(4)	C13	-	C14	-	O1	115.7(3)
				C15	-	C14	-	O1	124.5(3)
				C14	-	C15	-	C16	120.0(3)
				C11	-	C16	-	C15	120.1(4)
				C7	-	N1	-	C8	118.6(3)
				C8	-	N2	-	C9	119.5(3)
				C8	-	N2	-	N4	117.9(3)
				C9	-	N2	-	N4	122.5(3)
				C8	-	N3	-	C11	128.8(3)
				C14	-	O1	-	C17	117.9(3)

The rearrangement occurring in the reaction of 1-amino-2-methylthiopyrimidinium iodides **4** with hydrazines must follow an ANRORC mechanism involving as open-chain intermediate the azatriene **8** [7]. Either the hydrazine attacks position 6 of the educts **4** giving after ring opening isothiourea intermediates **8**, or substitution products **5** are primarily formed rearranging by an attack of the nucleophile upon position 6. Similar ring transformations have been found in reactions of quinazolinone [8-11] and 1,2,4-triazinone derivatives [12] with hydrazines or under hydrolytic conditions.

X-ray Structure Analysis.

Crystals of **6d** are monoclinic, space group $P2_1/n$ with 4 molecules in a unit cell of dimensions a = 13.690(2), b = 11.577(1), c = 11.212(4) Å and β = 98.21(2)°; V = 1759(1) Å^3; d_{calc} = 1.36 gcm^{-3}.

A number of 5324 intensities were measured on a *NONIUS CAD4* diffractometer using graphite monochromatized MoKα radiation; 2050 were below the 2.5σ level and were treated as unobserved. The structure was solved in a straightfoward application of the symbolic-addition program system *SIMPEL* [5] and refined by means of block-diagonal least-squares calculations, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms which were located in a ΔF-synthesis. An empirical absorption correction was applied [6]. The anomalous scattering was taken into account and a weighting scheme w = 1/(5.4 + F_o + 0.025F_o^2) was employed. An extinction correction was applied. The final R-value was 0.039 (R_w = 0.069) for the 3274 observed reflections. A picture of the molecule showing the atomic numbering is given in Figure 1. The bond distances and angles are listed in Table 1. The three six-membered rings C(1)-C(6), C(7)-C(10) and C(11)-C(16) are planar with maximum deviations of 0.005, 0.031 and 0.011 Å respectively from their best planes.

EXPERIMENTAL

1-Aryl-2(1*H*)-pyrimidinethiones **3**. General Procedure.

Arylamine **2** (10 mmoles) was added to a suspension of 3-isothiocyanato-2-propeniminium perchlorate **1** [2,4] (10 mmoles) in ethanol (10 ml). The mixture was briefly heated to boiling. After allowing to stand at room temperature for 30 minutes product **3** was filtered by suction and recrystallised.

1-Aryl-2-methylthiopyrimidinium Iodides **4**. General Procedure.

A mixture of **3** (10 mmoles), acetonitrile (20 ml) and iodomethane (2.13 g, 10 mmoles) was refluxed for 5 minutes. Unless product **4** precipitates from the cold solution, some diethyl ether (3-8 ml) will be added. The product was filtered by suction and recrystallised.

Table 2
1-Aryl-2(1*H*)-pyrimidinthiones **3** and 1-Aryl-2-methylthiopyrimidinium Iodides **4**

Product	Yield %	Mp °C [a]	Molecular Formula	Analysis % Calcd./Found C	H	N	MS (70 eV [b] m/z %	^{1}H-NMR (DMSO-d_6/TMS) [c] δ, J (Hz))
3a [d]	96	223-224 (Acetonitrile)	$C_{17}H_{14}N_2OS$ (294.4)	69.36 69.03	4.79 4.91	9.52 9.60		
3b	79	201-203 (Ethanol)	$C_{17}H_{14}N_2S$ (278.4)	73.35 73.35	5.07 5.25	10.06 9.81	279 (42), 278 (M^+, 100), 263 (8), 138 (12), 115 (21), 77 (29)	2.6 (s, 3H, CH_3), 7.57 (d, 2H, J = 8, C_6H_4) 7.68 (s, 5H, C_6H_5), 7.73 (s, 1H, J = 7, CHCN), 8.35 (d, 2H, J= 8, C_6H_4), 8.55 (d, 1H, J = 7, CHN)
3d	89	188-190 (Ethanol)	$C_{18}H_{16}N_2OS$ (308.4)	70.10 70.38	5.23 5.37	9.08 8.89		
3e [e]	70	235-237 (Acetonitrile)	$C_{17}H_{13}BrN_2S$ (357.3)	57.15 57.14	3.37 3.43	7.84 7.86	357 (M^+, 39), 355 (37), 276 (17), 235 (12), 178 (19), 177 (20), 128 (19), 115 (100), 102 (11), 91 (45), 89 (32), 75 (48) 303 (M^+, 44), 302 (86)	2.41 (s, 3H, CH_3), 7.40 (d, 2H, J = 8.3, C_6H_4), 7.44 (d, 2H, J = 8.8), 7.56 (d, 1H, J = 7, CHCN), 7.75 (d, 2H, J = 8.8, C_6H_4), 8.16 (d, 2H, J = 8.3, C_6H_4), 8.38 (d, 1H, J = 7, CHN)
3f [f]	68	318-320 (Acetonitrile)	$C_{18}H_{13}N_3S$ (303.4)	71.26 70.90	4.32 4.40	13.85 24.02	303 (M^+, 44), 302 (86), 288 (25), 152 (18), 129 (27), 115 (100), 102 (96) 91 (27), 89 (25), 75 (35)	2.43 (s, 3H,, CH_3), 7.53 (d, 2H, J = 8.4, C_6H_4), 7.71 (d, 1H, J = 7, CHCN), 7.71-8.05 (m, 4H), 8.21 (d, 2H, J = 8.4, C_6H_4), 8.57 (d, 1H, J = 7, CHN)
3g [g]	76	201-203 (Acetonitrile)	$C_{17}H_{13}ClN_2OS$ (328.8)	62.10 61.94	3.99 4.09	8.52 8.66	303 (M^+, 14), 327 (17) 137 (10), 136 (11), 102 101 (14), 92 (25), 77 (31), 75 (18), 15 (100) 303 (M^+, 44), 302 (86)	3.83 (s, 3H, OCH_3), 7.05 (d, 2H, J = 8.8), 7.39 (d, 2H, J = 8.8, C_6H_4), 7.56 (d, 1H, J = 7, CHCN), 7.65 (d, 2H, J = 8.8, C_6H_4), 8.25 (d, 2H, J = 8.8, C_6H_4), 8.41 (d, 1H, J = 7, CHN)
4a [h]	94	195-197 (Acetonitrile)	$C_{18}H_{17}IN_2OS$ (436.3)	49.55 49.73	3.93 4.02	6.42 6.31		
4b	87	188-193 (dec.) (Acetic acid)	$C_{18}H_{17}IN_2S$ (420.3)	51.44 51.74	4.01 4.26	6.67 6.39	277 (M^+ -CH_3I, 92), 142 (67), 115 (65), 91 (21), 77 (100), 15 (76)	2.67 (s, 3H, CH_3), 3.04 (s, 3H, SCH_3), 7.75 (d, 2H, J = 8, C_6H_4), 8.01 (s, 5H, C_6H_5), 8.7 (d, 2H, J = 8, C_6H_4), 8.77 (d, 1H, J = 7, CHNH), 9.47 (d, 1H, J = 7, CHN)
4d	91	197-199 (Acetonitrile)	$C_{19}C_{19}IN_2OS$ (450.3)	50.68 50.33	4.25 4.39		309 (18), 308 (M^+ -CH_3I, 66), 307 (100), 293 (15), 154 (13), 142 (99), 127 (58), 115 (43), 92 (24), 77 (29), 15 (47)	2.48 (s, 3H, CCH_3), 2.81 (s, 3H, SCH_3), 3.89 (s, 3H, OCH_3), 7.27 (d, 2H, J = 9.3), 7.53 (d, 2H, J = 8.3, C_6H_4), 7.75 (d, 2H, J = 9.3, C_6H_4), 8.48 (d, 2H, J = 8.3, C_6H_4), 8.53 (d, 1H, J = 6.8, CHCN), 9.23 (d, 1H, J = 6.8, CHN)
4e	83	215-217 (Acetonitrile)	$C_{18}C_{18}BrIN_2S$ (499.2)	43.31 43.54	3.23 3.38		371 (7), 357 (M^+ -CH_3I, 100), 355 (96), 276 (70), 230 (18), 228 (19), 178 (19), 177 (19), 142 (18), 133 (40), 128 (69), 127 (57), 115 (34), 91 (25), 82 (60), 80 (61)	2.48 (s, 3H, CH_3), 2.83 (s, 3H, SCH_3), 7.54 (d, 2H, J = 8.3), 7.77 (d, 2H, J = 7.8, C_6H_4), 8.01 (d, 2H, J = 7.8, C_6H_4), 8.52 (d, 2H, J = 8.3, C_6H_4), 9.25 (d, 1H, J = 6.7, CHN)
4f	80	197-200 (Acetonitrile)	$C_{19}C_{19}IN_3S$ (445.3)	51.25 51.63	3.62 3.85	9.44 9.13	303 (M^+ -CH_3I, 52), 302 (100), 288 (26), 142 (68), 129 (15), 127 (44), 115 (51), 102 (50), 91 (14)	2.5 (s, 3H, CCH_3), 2.91 (s, 3H, SCH_3), 7.57 (d, 2H, J = 8.3), 8.10 - 8.20 (m, 3H), 8.33 - 8.41 (m, 1H), 8.53 (d, 2H, J = 8.3), 8.73 (d, 1H, J = 7.3, CHCN), 9.47 (d, 1H, J = 7.3, CHN), 9.47
4g	80	185-202 (Acetonitrile)	$C_{16}C_{16}IN_3OS$ (470.8)	45.93 45.68	3.42 3.61	5.95 6.15	328 (M^+ -CH_3I, 19), 327 (25), 189 (5), 142 (100), 139 (10), 127 (60), 92 (15), 77 (17), 64 (19), 63 (16), 51 (10), 15 (96)	

[a] Uncorrected, measured with a Boetius heating block. [b] Obtained on a Varian MAT CH-6 spectrometer. [c] Recorded on a Tesla BS 587/C (80 MHz) spectometer. [d] UV (acetonitrile): λ max (log ε) = 249 (4.29), 279 (4.22), 312 sh (3.69), 382 (3.29) nm. [e] UV (dichloromethane): λ max (log ε) = 309 (4.65), 414 (3.39) nm. [f] UV (dichloromethane): λ max (log ε) = 307 (4.56), 414 (3.34) nm. [g] UV (dichloromethane): λ max (log ε) = 304 (4.67), 423 (3.36) nm. [h] UV (acetonitrile): λ max (log ε) = 248 (4.38), 311 (4.45) nm.

Table 3

1-Amino-2-arylaminopyrimididinium Iodides **6** and 1-Amino-2(1*H*)-pyrimidinimines **7**

Product	Yield %	mp °C [a] (solvent)	Molecular Formula	C	H	N
6a	89	163-165 (Acetonitrile)	$C_{17}H_{17}IN_4O$ (420.2)	48.59 48.67	4.08 4.20	13.3 13.50
6b	91	174.175 (Acetonitrile)	$C_{17}H_{17}IN_4$ (404.3)	50.51 50.19	4.24 4.42	13.86 13.94
6c	98	183-185 (Ethanol)	$C_{23}H_{21}IN_4$ (480.3)	57.51 57.73	4.41 4.22	11.66 11.72
6d [b]	87	217-219 (Acetonitrile)	$C_{18}H_{19}ClN_4O_5$ (406.8)	53.14 53.48	4.71 4.82	13.77 14.01
6e	89	165-173 (dec.) (Ethanol)	$C_{17}H_{16}BrIN_4$ (483.2)	42.26 42.06	3.34 3.45	11.60 11.50
6g	93	169-171 (Ethanol)	$C_{17}H_{16}ClIN_4O$ (454.7)	44.91 45.16	3.55 3.80	12.32 12.35
6i	73	176-177 (Ethanol)	$C_{24}H_{23}IN_4O$ (510.4)	56.43 56.35	4.51 4.66	11.00 10.8
7d	73	173-175 (Acetonitrile)	$C_{18}H_{18}N_4O$ (306.4)	70.57 70.40	5.92 6.10	18.29 17.95
7f	70	150-152 (Ethanol)	$C_{18}H_{15}N_5$ (301.4)	71.74 71.44	5.02 4.98	23.24 23.58
7h	88	198-200 (Ethanol)	$C_{24}H_{20}N_4O$ (380.5)	75.77 75.66	5.29 5.53	14.73 14.60

[a] Uncorrected, measured with a Boetius heating block. [b] Perchlorate! Obtained by dissolving free base **7d** in acetonitrile perchloric acid and diluting with ether.

Table 4

Spectroscopic Data of 1-Amino-2-arylaminopyrimidinium Iodides **6** and 1-Amino-2(1H)-pyrimidinimines **7**

Compound	MS (70 eV) [a] m/z %	UV [b] (CH_2CH_2) λ max (nm) (log ε)	^{1}H-NMR (DMSO-d_6/TMS) δ, J (Ha) [c]
6a	292 (M^+ -HI, 6), 277 (50), 262 (43), 254 (22), 155 (36), 133 (17), 128 (26), 127 (66), 121 (71), 103 (66), 77 (84), 63 (41), 51 (70), 28 (47), 15 (100)	300 (4.41) 379 (3.63)	
6b	276 (M^+ -HI, 6), 260 (100), 115 (12), 91 (10), 77 (11)	242 (4.27), 272 (4.20), 328 (4.41), 370 sh (3.83)	2.55 (s, 3H, CH_3), 7.31 (s, 2H, NH_2), 7.57 (d, 2H, J = 8, C_6H_4), 7.69-7.97 (m, 5H, C_6H_5), 8.06 (d, 1H, J = 7, CHCN), 8.24 (d, 2H, J = 8, C_6H_4), 8.99 (d, 1H, CHN, J = 7), 10.81 (s, 1H, NH)
6c [d]	352 (M^+ -HI, 11), 261 (50), 260 (100), 254 (16), 93 (31)	269 (4.21), 333 (4.46), 383 sh (3.80)	2.61 (s, 3H, CH_3), 7.27 (d, 2H, J = 8, C_6H_4), 7.5-8.0 (m, 10H, 2 C_6H_5), 8.16 (d, 1H, J = 7, CHCN), 8.37 (d, 2H, J = 8, C6H4), 9.04 (d, 1H, J = 7, CHN), 10.25 (s, 1H, NH), 11.41 (s, 1H, NH)
6e	354 (92), 340 (24), 338 (20), 260 (11), 254 (24), 169 (19), 143 (23), 142 (21), 130 (52), 128 (26), 127 (100), 102 (22), 91 (87), 90 (48), 89 (46)	293, 325, 379 sh [e]	2.40 (s, 3H, CH_3), 6.96 (s, 2H, NH_2), 7.40 (d, 2H, J = 8.3, C_6H_4), 7.62 (s, 4H, C_6H_4), 7.70 (d, 1H, J = 6.8, CHCN), 8.05 (d, 2H, J =8.3, C_6H_4), 8.65 (d, 1H, J = 6.8, CHN), 10.75 (br, 1H, NH)
6g	326 (M^+ -HI, 2), 311 (17), 296 (15), 254 (18), 137 (16), 127 (64), 121 (60), 105 (17), 102 (26), 75 (28), 61 (32), 28 (41), 15 (100)	297 sh (4.37), 317 (4.43) 380 (3.63)	3.80 (s, 3H, OCH_3), 6.85 (s, 2H, NH_2), 6.98 (d, 2H, J = 8.8, C_6H_4), 7.48 (d, 2H, J = 8.8, C_6H_4), 8.49 (d, 1H, J = 6.6, CHCN), 7.67 (d, 2H, J = 7.8, C_6H_4), 8.10 (d, 2H, J = 7.8, C_6H_4), 8.55 (d, 1H, J = 6.6, CHN), 10.75 (br, 1H, NH)
6i	382 (M^+ -HI, 15), 291 (97), 290 (78), 276 (93), 127 (69), 115 (90), 93 (84), 91 (78) 65 (100), 39 (89), 15 (70)		2.42 (s, 3H, CCH_3), 3.82 (s, 3H, OCH_3), 6.88[7.55 (m, 12 H, C_6H_4, C_6H_5, CHCN), 7.97 (d, 2H, J = 8.3, C_6H_4), 8.65 (d, 1H, J = 7, CHN)
7d	306 (M^+, 20), 291 (34), 276 (10), 248 (11), 121 (100), 28 (77)	295 (4.52), 431 (3.26)	2.35 (s, 3H, CCH_3), 3.73 (s, 3H, OCH_3), 6.35 (s, 2H, NH_2), 6.60 (d, 1H, J = 7, CHCN), 6.83 (d, 2H, J = 8, C_6H_4), 7.27 (d, 4H, J = 9, C_6H_4), 7.90 (d, 2H, J = 8, C_6H_4), 8.05 (d, 1H, J = 7, CHN)
7f	301 (M^+, 45), 285 (25), 260 (16), 185 (52), 157 (26), 143 (43), 128 (63), 116 (74), 115 (100), 102 (77), 91 (66), 89 (53), 77 (40), 29 (45), 27 (32)	299 (4.42), 329 sh (4.24), 380 (3.63)	2.36 (s, 3H, CH3), 6.68 (s, 2H, NH2), 6.94 (d, 1H, J = 7, CHCN), 7.01-7.1 (m, 1H, C_6H_4), 7.31 (d, 2H, J = 8.3, C_6H_4), 7.43-7.76 (m, 3H, C_6H_4), 7.93 (d, 2H, J = 8.3, C_6H_4), 8.27 (d, 1H, J = 7, CHN)
7h	380 (M^+, 6), 288 (63), 261 (52), 260 (100), 115 (21), 105 (50), 103 (18), 91 (16), 77 (64), 51 (22)		

[a] Obtained on a Varian MAT CH-6 spectrometer. [b] Recorded on a UV-Specord Carl-Zeiss-Jena Spectrophotometer. [c] Recorded on a Tesla BS 587/C (80 MHz) spectrometer. [d] UV (Acetonitrile): max (log ε) = 247 (4.40), 322 (4.460 nm. [e] Qualitative.

1-Amino-2-arylaminopyrimidinium Iodides **6** and 1-Amino-2(1*H*)-pyrimidinimines **7**. General Procedure.

Hydrazine hydrate (50%, 0.93 g, 12 mmoles) was added to a suspension of salt **4** in ethanol (30 ml). After allowing to stand for 5 minutes the mixture was refluxed for 5 minutes. After cooling down to room temperature the product precipitated. It was filtered by suction and recrystallised.

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