Synthesis of Pyrimidines from 3-Trifluoromethylsulfonyloxypropeniminium Triflates and Nitriles; Molecular and Crystal Structure of the 1:1 and 1:2 Adducts of a 4-(2-Diethylaminovinyl)pyrimidine with Triflic Acid†

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Received November 20, 1995

The 3-trifluoromethylsulfonyloxy-1-hexeniminium triflate **1** reacts with two equivalents of an aliphatic nitrile or of benzonitrile to give the 4-(2-diethylaminovinyl)pyrimidinediium bis(triflates) **4**, which can be deprotonated to give the monoprotonated or neutral pyrimidines **5** and **6**, respectively. When the related 1-phenyl-substituted iminium salt **7** is heated in acetonitrile at 140°, 1,5-cyclization of the cation leading to indane derivative **8** competes with formation of the pyrimidinium salt **9**. X-ray crystal structure determination reveals significant differences in the bond lengths of mono-and diprotonated 4-(2-diethylaminovinyl)pyrimidines **5a** and **4a**.

J. Heterocyclic Chem., **33**, 439 (1996).

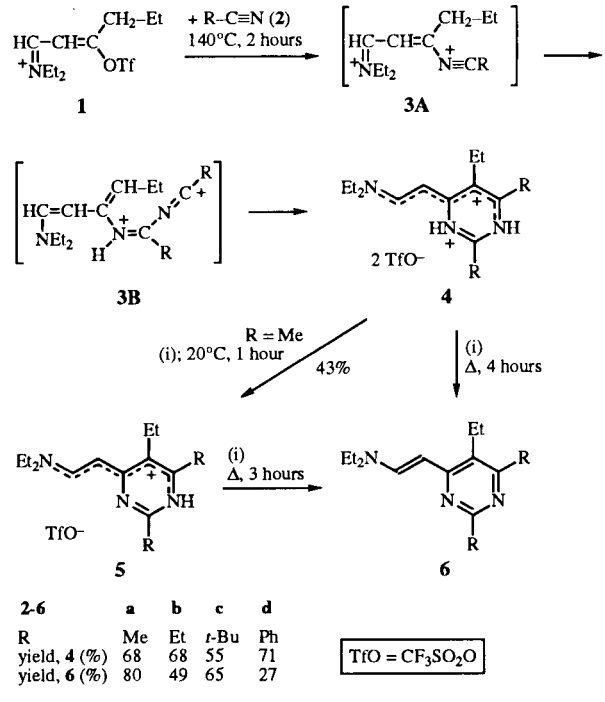
The pyrimidine ring can be assembled from various C_2 and two nitrile units [1]. Recently developed syntheses of this kind are based on the rapid nucleophilic addition of nitriles to short-lived carbenium ions, such as vinyl cations [2] or trifloxycarbenium ions (trifloxy = trifluoromethylsulfonyloxy) generated from enolizable ketones and trifluoromethanesulfonic (triflic) anhydride [3]. Our own investigations on 3-trifloxypropeniminium triflates revealed the highly electrophilic nature of this class of resonance-stabilized carbenium ions, as exemplified by their reactions with imines [4] and by intra- [5] or intermolecular [6] attack of arene systems. Therefore, we were curious to see whether these salts would be electrophilic enough to react with nitriles. This paper shows that this is indeed the case for appropriately substituted 3-trifloxypropeniminium salts.

Results.

When a solution of salt **1** (*E/Z* mixture) in an excess of nitriles **2a-d** is heated for 2 hours at 140° in a Schlenk pressure tube, the intensely yellow or orange-red pyrimidinediium bis(triflates) **4a-d** are formed. These hygroscopic salts can be isolated and fully characterized spectroscopically and structurally (see below). Their twofold deprotonation yields the 4-(2-diethylaminovinyl)pyrimidines **6a-d**. Under controlled conditions, the deprotonation sequence can also be carried out stepwise; thus, treatment of **4a** with aqueous sodium bicarbonate in a two-phase system at room temperature affords the pyrimidinium triflate **5a**, which is then transformed into **6a** at reflux temperature but under otherwise analogous conditions. Efforts to prepare pyrimidines from **1** and trimethylsilyl cyanide, acrylonitrile, 3-chloropropionitrile, and succinodinitrile were not successful.

We have recently shown that salt **7**, when heated at 150° without solvent, undergoes intramolecular electrophilic aromatic substitution which ultimately leads to

Scheme 1. Reaction of salt **1** with nitriles. Conditions: (i) $CH_2Cl_2/NaHCO_3$, H_2O



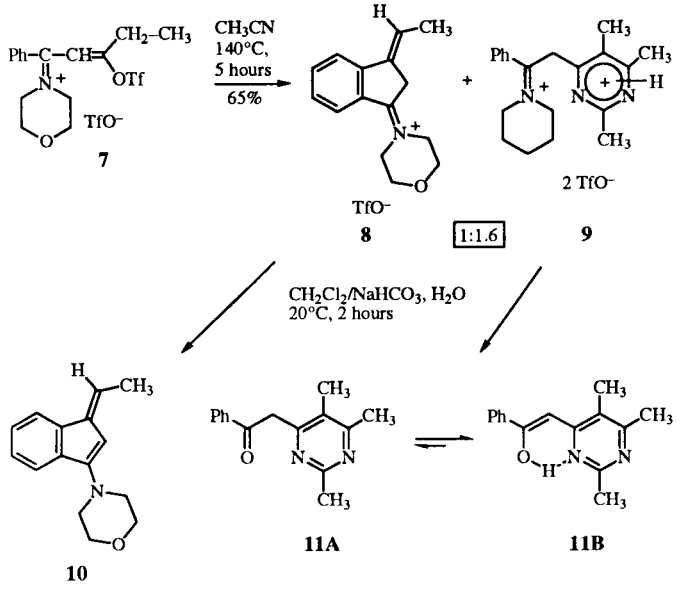
2-6	a	b	c	d
R	Me	Et	*t*-Bu	Ph
yield, **4** (%)	68	68	55	71
yield, **6** (%)	80	49	65	27

TfO = CF_3SO_2O

indanylidenemorpholinium triflate **8** in 87% isolated yield [5]. When **7** is heated in acetonitrile solution at 140°, however, the nitrile competes efficiently with the aromatic nucleus, and a 1:1.6 mixture of **8** and the pyrimidinium salt **9** is obtained. Although the two salts could not be separated, they were readily identified by their ^1H and ^{13}C nmr spectra (see Experimental). It should be noted that the dicationic salt **9** is a tautomer of the N^1,N^3-diprotonated pyrimidines **4**; obviously the N^1,C^7-diprotonated form is the more stable one in this specific case. Hydrolysis of the **8/9** mixture and chromatographic workup, accompanied by a significant loss of material,

provides the neutral pyrimidine derivative **11** besides the morpholinoindene **10**. In chloroform solution at 36°, the pyrimidine exists as a mixture of the ketone and enol tautomers **11A,B** in a 1:5.4 ratio [7].

Scheme 2



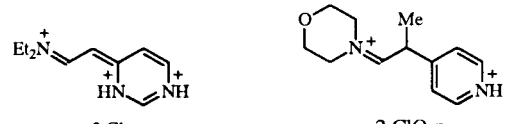
By analogy with the mechanism proposed for pyrimidine formation from trifloxycarbenium ions and nitriles [3], it can be assumed that the formation of pyrimidinium salt **4** proceeds *via* the nitrilium salt intermediates **3A** and **3B**. While **3B** is the logical precursor of **4**, in agreement with related 1,5-cyclization reactions where one of the termini is the carbon atom of a nitrilium function [2,3,8,9], the participation of **3A** is still speculative. Instead of conjugate addition of a nitrile molecule to salt **1** followed by HOTf elimination, the order of events may be reversed. We have shown that a variety of 3-trifloxypropeniminium triflates related to **1** and **7** (but mostly with 3-aryl instead of 3-alkyl substituents) undergo thermal HOTf elimination from the cation to form propyniminium triflates [5,9]. However, when **1** is subjected to vacuum thermolysis at 160°, unspecified decomposition occurs with no hint to the formation (by HOTf elimination) of the salts **12** or **13**; on the other hand, thermolysis at 130° in the presence of anthracene does furnish a product that is the formal [4+2] cycloaddition product of propyniminium salt **12** [5]. The observation that a propyniminium salt related to **12** (piperidino instead of dimethylamino, phenyl instead of propyl) does not react with acetonitrile at 140°, does not exclude the participation of **12** in the formation of **4**, but renders it less likely at least.

Formula 3

12 **13**

The occurrence of diprotonated forms **6** and **9** of 4-(2-aminovinyl)pyrimidines is not without precedent and analogy. Bredereck *et al.* have reported the preparation of 4-(dimethylaminovinyl)pyrimidine from 4-methylpyrimidine and chloromethylene-dimethylammonium chloride [11]. In the course of this synthesis, a salt was obtained which was transformed without further characterization into the final product by neutralization. Based on mechanistic considerations, structure **14** was assigned. The preparation of salts **4** suggests, however, that this salt was in reality also an adduct of the respective pyrimidine with two rather than three acid molecules. In a related synthesis, Liebscher *et al.* have obtained diperchlorates of 4-(2-dialkylaminovinyl)pyridines [12]. Besides the form protonated at the two nitrogen atoms, the N,C-diprotonated salt **15**, which structurally resembles our salt **9**, could be observed by nmr in water-containing DMSO solution.

Formula 4



14 **15**

Structures of **4a** and **5a**.

The structures of salts **4a** and **5a** have been determined by single-crystal X-ray diffraction. Crystal data are given in Table 1, atomic coordinates in Tables 2 and 3, and bond lengths as well as bond angles in Tables 4 and 5. It was found that salt **4a** contains a pyrimidine ring protonated at the two nitrogen atoms (Figure 1), whereas **5a** is monoprotonated at N-1 (Figure 2). In both salts, the trifluoromethanesulfonate counterions are associated with the cation by N-H···O hydrogen bonds.

By analogy to the protonation [13,14] and alkylation [15] of 4-aminopyrimidines, the first protonation of the vinylogous 4-(aminovinyl)pyrimidines **6** takes place at N-1. In this case, extended delocalization of the positive charge with participation of the exocyclic aminovinyl group is possible. In fact, partial bond length equalization is observed for the pentamethinecyanine unit between N-1 and N-2; in comparison with the bond lengths in pyrimidine itself [16], the deviations towards a more localized bond structure in this part of the ring are smaller than in the N1-C2-N3-C4 fragment. The cation is thus adequately described as a resonance hybrid as suggested by formula **5**. A similar bond length

Table 1

Crystal and Refinement Data for **4a** and **5a**

	4a	**5a**
formula	$C_{16}H_{25}F_6N_3O_6S_2$	$C_{15}H_{24}F_3N_3O_3S$
formula weight	533.5	383.4
F(000)	552	1616
crystal system	triclinic	monoclinic
space group	P $\bar{1}$	C2/c
a, Å	10.061(5)	27.740(6)
b, Å	11.632(6)	9.115(2)
c, Å	11.949(3)	19.369(4)
α, deg	66.00(4)	90
β, deg	75.03(3)	130.83(3)
γ, deg	81.31(3)	90
V, Å^3	1232.5(9)	3705.7(14)
Z	2	8
density (calc), g/cm^3	1.438	1.375
crystal dim, mm	0.50 x 0.65 x 0.50	0.80x0.55x0.30
μ, absorption coef, mm^{-1}	0.296	0.222
radiation	Mo-Kα	Mo-Kα
2Theta (max), deg	49.96	48.50
temperature, K	293	183
unique date	4319	2979
unique data, I > 2 σ(I)	3159	2211
Parameters refined	306	323
R1 [a]	0.0698	0.0396
wR2 [b]	0.1950	0.1041
GoF [c]	1.076	1.004

[a] R1 = $\sum$||Fol-| Fcll/$\sum$ |Fol. [b] wR2 = [$\sum$ [w(F_o^2-F_c^2)^2]/$\sum$ [w(Fo^2)^2]]$^{1/2}$. [c] GoF = [$\sum$ [w(F_o^2-F_c^2)^2]/(number of reflections-number of refined parameters)]$^{1/2}$.

Table 2

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å x 10^3) for **4a**

	x	y	z	U(eq)*
S(1)	435(1)	2422(1)	1474(1)	77(1)
S(2)	3878(1)	6474(1)	-6270(1)	80(1)
F(1)	1825(8)	1416(6)	-37(7)	218(3)
F(2)	524(6)	167(3)	1564(7)	206(3)
F(3)	-351(8)	1541(5)	120(7)	234(3)
F(4)	2417(5)	7896(4)	-7858(4)	154(2)
F(5)	1900(4)	8114(5)	-6109(5)	167(2)
F(6)	3672(6)	8888(4)	-7404(6)	192(2)
O(1)	441(3)	3616(3)	462(3)	93(1)
O(2)	-860(4)	2178(4)	2313(4)	143(2)
O(3)	1617(5)	2149(5)	1986(5)	141(2)
O(4)	4287(4)	6622(4)	-5289(3)	104(1)
O(5)	2935(6)	5541(4)	-5869(5)	150(2)
O(6)	4941(5)	6433(5)	-7285(4)	156(2)
N(1)	2515(3)	5298(3)	-851(3)	56(1)
N(2)	7372(4)	8046(4)	-5135(3)	86(1)
N(3)	3889(3)	6204(3)	-2756(3)	52(1)
C(1)	2070(4)	4942(5)	-2582(4)	75(1)
C(2)	2847(3)	5495(3)	-2042(3)	52(1)
C(3)	2502(4)	5586(4)	1042(3)	70(1)
C(4)	4666(3)	6767(3)	-2328(3)	50(1)
C(5)	4194(4)	6601(3)	-1026(3)	54(1)
C(6)	3130(4)	5864(3)	-307(3)	54(1)
C(7)	5790(4)	7425(4)	-3120(3)	61(1)
C(8)	6376(4)	7391(4)	-4296(4)	69(1)
C(9)	7939(6)	9092(6)	-5005(5)	108(2)

Table 2 (conttinued)

	x	y	z	U(eq)*
C(10)	7050(10)	10268(7)	-5373(8)	154(3)
C(11)	7905(7)	7876(8)	-6335(6)	143(3)
C(12)	9068(12)	7057(15)	-6300(14)	286(9)
C(13)	4892(5)	7278(4)	-510(4)	75(1)
C(14)	4385(7)	8637(5)	-840(5)	109(2)
C(15)	612(9)	1330(6)	739(9)	132(3)
C(16)	2941(7)	7939(6)	-6971(6)	107(2)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Bond Lengths (Å) and Angles (deg) for **4a**

S(1)-O(2)	1.410(4)	S(1)-O(3)	1.412(4)
S(1)-O(1)	1.423(3)	S(1)-C(15)	1.782 (8)
S(2)-O(5)	1.400(5)	S(2)-O(6)	1.407(4)
S(2)-O(4)	1.417(3)	S(2)-C(16)	1.804(7)
F(1)-C(15)	1.317(9)	F(2)-C(15)	1.311(8)
F(3)-C(15)	1.303(8)	F(4)-C(16)	1.320(7)
F(5)-C(16)	1.322(7)	F(6)-C(16)	1.268(7)
N(1)-C(2)	1.305(4)	N(1)-C(6)	1.384(4)
N(1)-H(1)	0.69(4)	N(2)-C(8)	1.296(5)
N(2)-C(11)	1.478(7)	N(2)-C(9)	1.495(6)
N(3)-C(2)	1.317(4)	N(3)-C(4)	1.391(4)
N(3)-H(3)	0.76(4)	C(1)-C(2)	1.480(5)
C(3)-C(6)	1.488(5)	C(4)-C(7)	1.371(5)
C(4)-C(5)	1.444(5)	C(5)-C(6)	1.350(5)
C(5)-C(13)	1.510(5)	C(7)-C(8)	1.390(5)
C(9)-C(10)	1.487(10)	C(11)-C(12)	1.39(2)
C(13)-C(14)	1.506(8)		
O(2)-S(1)-O(3)	118.0(3)	O(2)-S(1)-C(15)	103.4(4)
O(3)-S(1)-C(15)	103.9(3)	O(1)-S(1)-C(15)	103.5(3)
O(5)-S(2)-O(6)	112.6(4)	O(5)-S(2)-O(4)	114.6(3)
O(6)-S(2)-O(4)	116.1(3)	O(5)-S(2)-C(16)	105.1(3)
O(6)-S(2)-C(16)	102.5(3)	O(4)-S(2)-C(16)	103.9(3)
C(2)-N(1)-C(6)	123.8(3)	C(8)-N(2)-C(11)	120.8(4)
C(8)-N(2)-C(9)	122.3(4)	C(11)-N(2)-C(9)	116.5(4)
C(2)-N(3)-C(4)	124.4(3)	N(1)-C(2)-N(3)	118.3(3)
N(1)-C(2)-C(1)	121.0(3)	N(3)-C(2)-C(1)	120.7(3)
C(7)-C(4)-N(3)	120.5(3)	C(7)-C(4)-C(5)	124.3(3)
N(3)-C(4)-C(5)	115.1(3)	C(6)-C(5)-C(4)	119.5(3)
C(6)-C(5)-C(13)	121.7(3)	C(4)-C(5)-C(13)	118.8(3)
C(5)-C(6)-N(1)	118.6(3)	C(5)-C(6)-C(3)	127.1(3)
N(1)-C(6)-C(3)	114.3(3)	C(4)-C(7)-C(8)	123.5(3)
N(2)-C(8)-C(7)	127.5(4)	C(10)-C(9)-N(2)	111.3(5)
C(12)-C(11)-N(2)	112.0(9)	C(14)-C(13)-C(5)	112.4(4)
F(3)-C(15)-F(2)	107.2(6)	F(3)-C(15)-F(1)	109.2(9)
F(2)-C(15)-F(1)	107.7(6)	F(3)-C(15)-S(1)	111.2(5)
F(2)-C(15)-S(1)	111.6(7)	F(1)-C(15)-S(1)	109.8(5)
F(6)-C(16)-F(4)	110.4(6)	F(6)-C(16)-F(5)	106.4(6)
F(4)-C(16)-F(5)	107.3(6)	F(6)-C(16)-S(2)	112.8(5)
F(4)-C(16)-S(2)	110.3(4)	F(5)-C(16)-S(2)	109.4(5)

pattern has been reported for 4-dimethylamino-1,2,6-trimethylpyrimidinium iodide [15] and 4-amino-1-methyl-2-(methylthio)pyrimidinium chloride [17].

In comparison with **5a**, the bond length alternation of the pentamethine unit in the diprotonated pyrimidine **4a** is more pronounced, the bonds N1-C6 and N3-C4 are longer, and the N1-C2 and N3-C8 bond lengths are approaching the value of a C=N double bond [18,19].

Table 4

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **5a**

	x	y	z	U(eq) *
S	1306(1)	1111(1)	5209(1)	33(1)
F(1)	374(1)	1708(3)	5180(2)	87(1)
F(2)	1187(1)	3101(2)	6064(2)	81(1)
F(3)	1216(1)	902(3)	6470(2)	78(1)
O(1)	1023(1)	2129(2)	4469(1)	49(1)
O(2)	1056(1)	-359(2)	4934(1)	48(1)
O(3)	1985(1)	1190(2)	5916(1)	47(1)
N(1)	-29(1)	-1998(3)	3542(2)	30(1)
N(2)	-2146(1)	-3605(2)	-558(1)	34(1)
N(3)	-899(1)	-1850(2)	1990(1)	29(1)
C(1)	-425(2)	407(3)	2851(2)	42(1)
C(2)	-457(1)	-1224(3)	2772(2)	29(1)
C(4)	-932(1)	-3363(3)	1944(2)	27(1)
C(5)	-527(1)	-4213(3)	2768(2)	29(1)
C(6)	-64(1)	-3495(3)	3565(2)	29(1)
C(7)	-1376(1)	-4001(3)	1078(2)	31(1)
C(8)	-1737(1)	-3145(3)	301(2)	30(1)
C(9)	-2282(2)	-5177(3)	-781(2)	43(1)
C(10)	-2759(2)	-5747(4)	-707(3)	54(1)
C(11)	-2491(1)	-2557(4)	-1315(2)	39(1)
C(12)	-2239(2)	-2517(5)	-1811(2)	54(1)
C(13)	-632(1)	-5846(3)	2754(2)	35(1)
C(14)	-1184(2)	-6158(4)	2729(3)	49(1)
C(15)	409(2)	-4185(4)	4486(2)	40(1)
C(16)	1008(2)	1733(4)	5758(2)	51(1)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5

Bond Lengths (Å) and Angles (deg) for **5a**

S-O(3)	1.433(2)	C(1)-C(2)	1.491(4)
S-O(1)	1.436(2)	C(4) -C(5)	1.437(4)
S-O(2)	1.441(2)	C(4)-C(7)	1.402(4)
S-C(16)	1.813(3)	N(3)-C(2)	1.302(3)
F(1)-C(16)	1.332(4)	N(3)-C(4)	1.381(3)
F(2)-C(16)	1.329(4)	C(5)-C(6)	1.366(4)
F(3)-C(16)	1.329(4)	C(5)-C(13)	1.514(4)
N(1)-C(2)	1.348(3)	C(6)-C(15)	1.496(4)
N(1)-C(6)	1.370(3)	C(7) -C(8)	1.381(4)
N(1)-H(1N)	0.83(3)	C(9)-C(10)	1.514(5)
N(2)-C(8)	1.327(3)	C(11)-C(12)	1.513(5)
N(2)-C(11)	1.464(4)	C(13)-C(14)	1.527(5)
N(2)-C(9)	1.473(4)		
O(3)-S-O(1)	116.11(14)	O(3)-S-O(2)	114.49(13)
O(1)-S-O(2)	114.54(13)	O(3)-S-C(16)	103.96(14)
O(1)-S-C(16)	102.9(2)	O(2)-S-C(16)	102.4(2)
C(2)-N(1)-C(6)	121.8(2)	C(8)-N(2)-C(11)	120.8(2)
C(8)-N(2)-C(9)	121.4(2)	C(11)-N(2)-C(9)	117.8(2)
C(2)-N(3)-C(4)	119.0(2)	N(3)-C(2)-N(1)	122.4(2)
N(3)-C(2)-C(1)	120.3(3)	N(1)-C(2)-C(1)	117.3(3)
N(3)-C(4)-C(7)	117.4(2)	N(3)-C(4)-C(5)	119.7(2)
C(7)-C(4)-C(5)	122.9(2)	C(6)-C(5)-C(4)	118.1(2)
C(6)-C(5)-C(13)	121.3(2)	C(4)-C(5)-C(13)	120.5(2)
C(5)-C(6)-N(1)	118.3(2)	C(5)-C(6)-C(15)	126.1(3)
N(1)-C(6)-C(15)	115.5(3)	C(8)-C(7)-C(4)	120.9(3)
N(2)-C(8)-C(7)	127.2(3)	N(2)-C(9)-C(10)	112.1(3)
N(2)-C(11)-C(12)	112.4(3)	C(5)-C(13)-C(14)	111.1(2)
F(3)-C(16)-F(2)	106.8(3)	F(3)-C(16)-F(1)	107.5(3)
F(2)-C(16)-F(1)	107.0(3)	F(3)-C(16)-S	112.0(2)
F(2)-C(16)-S	112.1(3)	F(1)-C(16)-S	111.1(2)

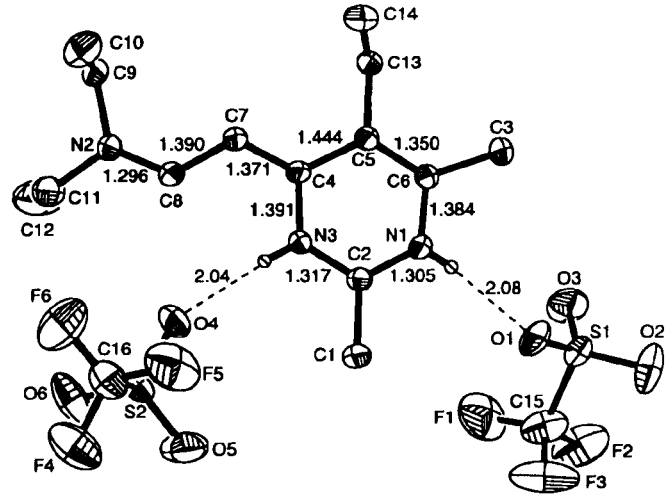


Figure 1. Molecular structure of salt **4a**; the esd's of the given bond lengths are 0.004-0.005 Å, except for O···H. Further bond lengths [Å]: N1-H1 0.69(4), N3-H3 0.76(4). Torsion angles [deg]: C4-C7-C8-N2 174.8, C5-C4-C7-C8 -168.1, N3-C4-C7-C8 -12.0, N3-C4-C5-C6 4.6, C4-C5-C6-N1, -0.6, C2-N1-C6-C5 -4.4, C6-N1-C2-N3 4.9, C4-N3-C2-N1 -0.3, C2-N3-C4-C5 -4.3, C2-N3-C4-C7 175.8.

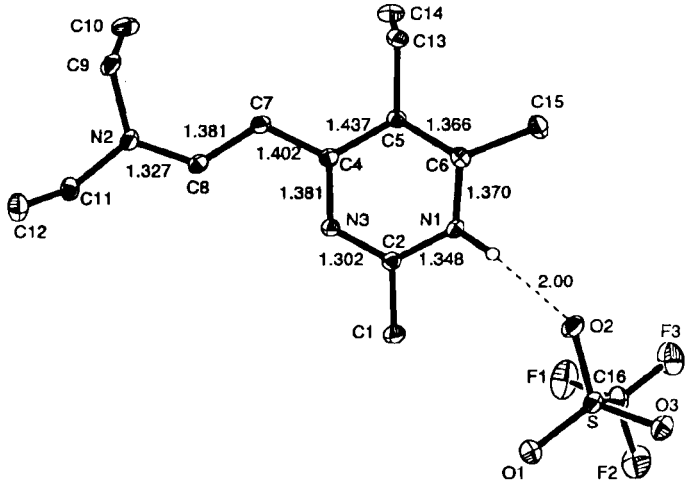
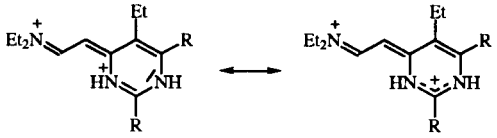


Figure 2. Molecular structure of salt **5a**; the esd's of the given bond lengths are 0.003-0.004 Å. Torsion angles [deg]: C4-C7-C8-N2 176.0, C5-C4-C7-C8 -177.2, N3-C4-C7-C8 3.9, N3-C4-C5-C6 173.0, C4-C5-C6-N1 2.9, C2-N1-C6-C5 3.7, C6-N1-C2-N3 -5.4, C4-N3-C2-N1 -0.1, C2-N3-C4-C5 6.7, C2-N3-C4-C7 -174.4.

Therefore, the bond structure in this cation is represented best by the resonance **4** ↔ **4'** with a major contribution of the latter that features an amidinium (N1-C2-N3) and a pentadieniminium unit (C6-C5-C4-C7-C8-N2). The pyrimidine rings in **4a** and in **5a** are not strictly planar (compare the torsion angles, Figures 1 and 2) but are deformed towards a boat form, with N3,C2,C5,C6 at the base and C4,N1 at the tips of the boat. When a least-squares plane is defined for the base atoms, these atoms

themselves deviate by ±0.003 Å (±0.007 Å) from this plane in **4a** (**5a**), and C4 and N1 are offset by 0.050 (0.080) and 0.045 (0.044) Å, respectively.

Formula 5



4 **4'**

NMR Spectra.

^{1}H nmr data of **4-6** are compiled in Table 6, ^{13}C nmr data in Table 7. For some of the assignments made for **6**, the studies on 4-aminopyrimidines, especially on 2,6-dimethyl-4-aminopyrimidine, were considered relevant (^{1}H [20], ^{13}C [21]). As in these compounds [13,22], the protonation at N-1, which has been established by the structure determinations of **4a** and **5a** (see above), increases the barrier of rotation at the C-N bond of the exocyclic aminovinyl function and consequently, two sets of NCH_2CH_3 signals are

Table 6

^{1}H NMR Data for Pyrimidine Derivatives **4**, **5**, and **6** [a,b] (δ/ppm)

Compound	7-H [c]	8-H [c]	NCH_2	NCH_2-CH_3	5-CH_2	5-CH_2-CH_3	Other signals [d]
4a	5.53	8.61	3.72, 3.79	1.32, 1.41	2.59	1.13	2.44 (s, 6-Me), 2.81 (s, 2-Me)
4b	5.56	8.54	3.73, 3.79	1.38, 1.43	2.60	1.13	1.25 (t, 3 H), 1.29 (t, 3 H), 2.72 (q, 6-CH_2), 3.04 (q, 2-CH_2)
4c [e]	5.65	8.46	3.75, 3.82	1.29, 1.38	3.13	1.18	1.52 (s, 9 H), 1.58 (s, 9 H), 9.51 (s, broad, NH), 11.17 (s, broad, NH)
4d	5.77	8.66	3.73, 3.84	1.33, 1.42	2.54	1.12	7.56-7.88 (m, 8 H), 8.05 (m_c, 2H)
5a	5.27	8.40	3.50	1.33	2.52	1.13	2.45 (s, 3 H), 2.57 (s, 3 H), 11.78 (s, broad, NH)
6a	5.16	7.90	3.32	1.20	2.54	1.12	2.38 (s, 6-Me), 2.52 (s, 2-Me)
6b	5.18	7.94	3.28	1.25	2.56	1.14	1.29 (t, 3 H), 1.33 (t, 3 H), 2.66 (q, 6-CH_2), 2.77 (q, 2-CH_2)
6c	5.24	7.99	3.26	1.20 or 1.18	2.77	1.18 or 1.20	1.36 (s, 9 H), 1.39 (s, 9 H)
6d	5.29	8.21	3.31	1.22	2.59	1.16	7.36-7.55 (m, 8 H), 8.49 (mc, 2H)

[a] Measured at 200.1 MHz **5a**, **6a** or 400.1 MHz. [b] Measured in deuterioacetonitrile **4b-d**, deuterioacetonitrile/deuteriochloroform (= 1 :1) **4a**, or deuteriochloroform **5a**, **6a-d**. [c] ^{3}J = 11.9-12.1 Hz for **4a-d**, **5a**, 12.7-12.8 Hz for **6a-d**. [d] The NH signal of **4a,b,d** was not found. [e] T = 253 K.

Table 7

^{13}C NMR Data for Pyrimidine Derivates **4**, **5**, and **6** [a] (100.6 MHz, δ/ppm, J/Hz)

Compound	C-2,-4,-6	C-5	C-7 (^{1}JC,H)	C-8 (^{1}JC,H)	5-CH_2	NCH_2	$CF_3SO_3^-$ (^{1}JC,F)	Other signals
4a	145.0, 150.9, 158.5	124.4	88.4 (163.0)	157.5 (185.3)	19.1	44.5 53.4	120.8 (319.3)	9.8 (CH_2CH_3), 11.4/13.0 (NCH_2CH_3), 15.7 (Me), 16.7 (Me)
4b	151.7, 152.7, 164.6	126.5	90.4 (163.7)	159.2 (172.4)	20.0	45.9 54.9	121.4 (319.8)	11.9/12.3/12.8/12.9/14.2 (Me), 24.5 (6-CH_2), 25.9 (2-CH_2)
4c [b]	166.7, 167.6, 172.7	127.4	91.2 (163.4)	159.6 (169.9)	20.6	45.3 54.5	121.2 (319.6)	11.5/12.5/13.8 (Me), 26.2/27.9 (CMe_3), 37.7/38.4 (CMe_3)
4d	146.8, 154.0, 157.5	125.5	92.3 (163.3)	159.9 (173.2)	21.2	46.0 54.8	121.4 (320.0)	12.0/12.8/14.0 (Me), 127.6-136.0 (C-aryl)
5a	149.5, 155.7, 166.0	121.7	90.0 (157.6)	154.0 (168.6)	19.3	43.3 51.7	120.3 (320.1)	11.4 (CH_2CH_3), 11.4/14.3(NCH_2CH_3), 16.3 (6-Me), 21.2 (2-Me)
6a	161.5 [c], 161.8, 162.5 [d]	122.2	88.6 (153.3)	145.0 (164.8)	19.9	45.5 [e]		12.4/12.7 (CH_2CH_3, NCH_2CH_3), 21.6 (6-Me), 25.4 (2-Me)
6b	162.1, 166.4, 166.8	121.7	89.2 (153.2)	144.9 (164.3)	19.5	45.6 [e]		12.5/12.8/13.4, 13.4 (CH_2CH_3, NCH_2CH_3), 27.5 (6-CH_2), 32.1 (2-CH_2)
6c	162.8, 170.4 (2 C?)	121.9	90.3 (152.6)	144.4 (164.7)	20.8	46.0 [e]		13.3 [e]/13.9 (CH_2CH_3), 29.6/30.5 (CMe_3), 38.9/39.2 (CMe_3)
6d	159.9, 163.6, 164.1	123.4	89.6 (153.7)	145.8 (164.9)	21.0	46.3 [e]		13.2 [e] (NCH_2CH_3), 14.0 (CH_2CH_3), 127.9, 128.6, 129.2, 139.2, 140.6

[a] Measured in deuterioacetonitrile **4b-d**, deuterioacetonitrile/deuteriochloroform (1:1) **4a**, or deuteriochloroform **5a**, **6a-d**. [b] T = 253 K. [c] ^{2}J(C, H) = 5.5 Hz. [d] ^{2}J(C, H) = 6.5 Hz. [e] Broadened signal.

observed in salts **4** and **5**. In the proton spectra measured at room temperature, the NH signals of the diprotonated salts **4** are not observed, but we could detect them as broad signals, when a spectrum of **4c** was registered at -20°. When methyl- and 4-aminopyrimidines are protonated, the ^{13}C nmr signals of the nuclei adjacent to the protonation side (N-1) are shielded (C-2, C-6 and 2-C, 6-C) and C-5 is deshielded, but the C-4 resonance in 4-aminopyrimidines is affected only to a small extent [23]. As far as assignments have been made (Table 7), these effects are also observed for salts **4** and **5**. For the signals C-2,-4,-6, which were not assigned in detail, a general high-field shift for the protonated species is observed with a few exceptions. The comparison of **4a, 5a**, and **6a** shows that the shielding of C-2, 4,-6 increases not only from the neutral to the monoprotonated but also from the latter to the diprotonated form. The same is true for the coupling constants ^1J(C-7, 7-H) and ^1J(C-8, H-8); this change is certainly due to charge delocalization in the pentamethinecyanine unit [24] as discussed above.

EXPERIMENTAL

The ^1H nmr were recorded on Bruker AC 200 (200.1 MHz) and Bruker AM 400 (400.1 MHz) instruments, with tetramethylsilane as internal standard. The ^{13}C nmr spectra were obtained on a Bruker AM 400 (100.6 MHz) instrument; the solvent signal was used as internal standard [δ (*C*DCl$_3$) 77.0, δ (CD$_3$*C*N) 118.2]. The ir spectra were recorded on a Perkin-Elmer 1310 spectrometer. Elemental microanalyses were carried out with a Perkin-Elmer EA 2400 instrument. Melting points were taken in a copper block, temperatures given are not calibrated.

4-[(*E*)-2-Diethylaminovinyl]-5-ethyl-2,6-dimethylpyrimidine-1*H*$^+$,3*H*$^+$-diium Bis(trifluoromethanesulfonate) (**4a**).

A solution of salt **1a** [25] (4.15 g, 9.19 mmoles) in acetonitrile (20 ml) was heated in a Schlenk pressure tube at 140° for 2 hours. The dark-red solution was concentrated to a volume of 10 ml. Upon cooling at -36°, orange-red hygroscopic crystals of **4a** separated, yield 3.34 g (68%), mp 190-192°; ir (potassium bromide): ν 3230-*ca.* 2500, 1650, 1610, 1290-1270/1245-1210/1180-1160/1030 (TfO$^-$) cm^{-1}.

Anal. Calcd. for $C_{16}H_{25}N_3F_6O_6S_2$ (533.5): C, 36.02; H, 4.72; N, 7.88. Found: C, 36.0; H, 4.7; N, 7.7.

4-[(*E*)-2-Diethylaminovinyl]-2,5,6-triethylpyrimidine-1*H*$^+$,3*H*$^+$-diium Bis(trifluoromethanesulfonate) (**4b**).

A solution of salt **1a** [25] (3.57 g, 7.91 mmoles) in propionitrile (10 ml) was heated in a Schlenk pressure tube at 140° for 2 hours. Back at room temperature, a red oil was separated by addition of ether which was isolated and dissolved in dichloromethane (20 ml). Upon cooling at -36°, **4b** was obtained as an orange-red hygroscopic powder, yield 3.04 g (68%), mp 110-112°; ir (potassium bromide): ν 3140 - *ca.* 2500, 1610, 1285-1210/1155/1025 (TfO$^-$) cm^{-1}.

Anal. Calcd. for $C_{18}H_{29}N_3F_6O_6S_2$ (561.6): C, 38.50; H, 5.21; N, 7.48. Found: C, 38.8; H, 5.2; N, 7.3.

2,6-Di-*tert*-butyl-4-(*E*)-2-diethylaminovinyl]-5-ethylpyrimidine-1*H*$^+$,3*H*$^+$-diium Bis(trifluoromethanesulfonate) (**4c**).

A solution of salt **1a** [25] (3.28 g, 7.27 mmoles) in pivalonitrile (10 ml) was heated in a Schlenk pressure tube at 140° for 2 hours. Back at room temperature, a red oil was separated by addition of ether which was isolated and dissolved in dichloromethane (20 ml). Ether was added until the solution became turbid. Upon cooling at -36°, a yellow precipitate of **4c** formed which was isolated and washed with ether (2 x 50 ml), yield 2.49 g (55%), mp 107-110°; ir (potassium bromide): ν 3380 (NH), 1600, 1290-1210/1155/1025 (TfO$^-$) cm^{-1}.

Anal. Calcd. for $C_{22}H_{37}N_3F_6O_6S_2$ (617.7): C, 42.78; H, 6.04; N, 6.80. Found: C, 42.8; H, 6.0; N, 6.7.

4-[(*E*)-2-Diethylaminovinyl]-5-ethyl-2,6-diphenylpyrimidine-1*H*$^+$,3*H*$^+$-diium Bis(trifluoromethanesulfonate) (**4d**).

A solution of salt **1a** [25] (6.36 g, 14.09 mmoles) in benzonitrile (20 ml) was heated in a Schlenk pressure tube at 140° for 2 hours. Back at room temperature, a red oil was separated by addition of ether (20 ml), which was purified further by dissolving in acetonitrile and precipitation with ether (2 x). After removal of the volatiles at 0.005 mbar, a hygroscopic orange-colored powder was obtained, yield 6.55 g (71%), mp 78-80°; ir (potassium bromide): ν 3240-2680, 1610, 1580, 1550, 1285/1255/1240/1160/1025 (TfO$^-$) cm^{-1}.

Anal. Calcd. for $C_{26}H_{29}N_3F_6O_6S_2$ (657.6): C, 47.49; H, 4.44; N, 6.39. Found: C, 46.8; H, 4.8; N, 6.1. The hemihydrate (**4d**•0.5H$_2$O) would require: C, 46.84; H, 4.54; N, 6.30.

4-[(*E*)-2-Diethylaminovinyl]-5-ethyl-2,6-dimethyl-1*H*$^+$-pyrimidinium Trifluoromethanesulfonate (**5a**).

The mixture obtained by addition of a saturated aqueous solution of sodium hydrogen carbonate (20 ml) to a solution of salt **4a** (3.79 g, 7.10 mmoles) in dichloromethane (30 ml) was stirred vigorously during 1 hour. The organic phase was separated, and the aqueous layer was extracted with dichloromethane (2 x 10 ml). From the organic phases, a crude product was obtained which was washed with ether (*ca.* 10 ml). This procedure yielded 1.16 g (43%) of **5a** as red-brown needles, mp 142°; ir (potassium bromide): ν 3250 (NH), 3120, 1610, 1578-1550, 1280-1250/1240/1215/1145/1020 (TfO$^-$) cm^{-1}.

Anal. Calcd. for $C_{15}H_{24}N_3F_3O_3S$ (383.4): C, 46.99; H, 6.31; N, 10.96. Found: C, 47.1; H, 6.2; N, 11.0.

General Procedure for Pyrimidine Derivatives **6a-d**.

A saturated aqueous solution of sodium hydrogen carbonate (10 ml) was added to a solution of salts **5a-d** (4-4.5 mmoles) in dichloromethane (20 ml), and this mixture was vigorously stirred at reflux temperature for 4 hours. The organic layer was separated, and the aqueous layer was extracted with 2 x 10 ml of dichloromethane. The combined organic phases were dried over magnesium sulfate, the solvent was removed, and the residue was subjected to a Kugelrohr distillation. The pyrimidines so obtained should be stored in an inert atmosphere, since they gradually deteriorate in contact with air. The nmr data are given in Tables 6 and 7.

4-[(*E*)-2-Diethylaminovinyl]-5-ethyl-2,6-dimethylpyrimidine (**6a**).

This compound was obtained as an orange-red oil, bp 200°/0.01 mbar (Kugelrohr), yield 80%; ir (film): ν 1605, 1550-1505 cm^{-1}.

Anal. Calcd. for $C_{14}H_{23}N_3$ (233.4): C, 72.06; H, 9.93; N, 18.01. Found: C, 71.5; H, 9.8; N, 18.0.

The compound was also obtained by treatment of salt **5a** with a saturated aqueous solution of sodium hydrogen carbonate at reflux temperature for 3 hours followed by workup as described above, yield 81%.

4-[(*E*)-2-Diethylaminovinyl]-2,5,6-triethylpyrimidine (**6b**).

This compound was obtained as an orange-colored oil, bp 190°/0.05 mbar (Kugelrohr), yield 49%; ir (film): ν 1610, 1540-1510 cm^{-1}.

Anal. Calcd. for $C_{16}H_{27}N_3$ (261.4): C, 73.52; H, 10.41; N, 16.07. Found: C, 73.2; H, 10.3; N, 15.8.

2,6-Di-*tert*-butyl-4-[(*E*)-2-diethylaminovinyl]-5-ethylpyrimidine (**6c**).

This compound was obtained as a viscous yellow oil, bp 200°/0.03 mbar (Kugelrohr), yield 65%; ir (film): ν 1595 (s), 1510-1490 (s, br) cm^{-1}.

Anal. Calcd. for $C_{20}H_{35}N_3$ (317.5): C, 75.66; H, 11.11; N, 13.23. Found: C, 75.5; H, 11.0; N, 13.0.

4-[(*E*)-2-Diethylaminovinyl]-5-ethyl-2,6-diphenylpyrimidine (**6d**).

Kugelrohr distillation at 250°/0.03 mbar yielded a viscous red oil which crystallized from ether at -36°, yield 27%, mp 95°; ir (film): ν 1615 cm^{-1}.

Anal. Calcd. for $C_{24}H_{27}N_3$ (357.5): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.3; H, 7.7; N, 11.5.

1-(*E*)-Ethylidene-3-morpholinoindene (**10**) and 2,5,6-Trimethyl-4-phenacylpyrimidine (**11**).

A solution of salt **7** [25] (2.51 g, 4.76 mmoles) in acetonitrile (10 ml) was heated in a Schlenk pressure tube at 140° during 5 hours. After cooling, an oil was separated by addition of ether (20 ml), which was isolated and dissolved in acetonitrile. At -36°, a crystalline mixture (1.56 g) of [(*E*)-3-ethyliden-1-indanylidene]morpholinium trifluoromethanesulfonate (**8**) [5] and [1-phenyl-2-(2,5,6-trimethylpyrimidinio-4-yl)ethylidene]morpholinium bis(trifluoromethansulfonate) (**9**) formed which could not be separated (ratio **9**/**8** = 1.6); for nmr data of **9**, see Tables 6 and 7.

A suspension of this mixture in dichloromethane (15 ml) was treated with a saturated aqueous solution of sodium hydrogen carbonate (5 ml) by vigorous stirring for 2 hours The layers are separated, the aqueous phase was extracted with dichloromethane (10 ml), and the organic layers were combined and dried. After concentration, the residue was fractionated by column chromatography on silica gel (30 g). Eluation with ether-light petroleum (1:1, 300 ml) yielded **10** [5] which was recrystallized from ether, yield 68 mg (6%). Further eluation with acetonitrile (100 ml) provided 0.25 g (22%) of **11** as beige crystals, mp 121°; ir (potassium bromide): ν 1620 (C=O), 1560 cm^{-1}; ^1H nmr (deuteriochloroform, 400.1 MHz): ketone **11A** and enol form **11B**, 1:5.4; **11A**: δ 2.13 (s, 5-Me), 2.46 (s, 6-Me), 2.62 (s, 2-Me), 4.47 (s, CH_2); **11B**: δ 2.12 (s, 5-Me), 2.40 (s, 6-Me), 2.55 (s, 2-Me), 6.0 (s, =CH), 16.6 (s, OH); common signals of **11A** and **B**: δ 7.41-7.57/7.86-8.04 (m, 5H); ^{13}C nmr (deuteriochloroform, 100.6 MHz): **11A**: δ 13.8 (5-Me), 22.4 (Me), 25.4 (Me), 46.2 (CH_2), 125.1 (C-5), 126.2, 128.2, 130.2, 138.0, 161.2, 164.1, 165.3, 195.3 (C=O); **11B**: δ 12.7 (5-Me), 22.5 (Me), 23.5 (Me), 86.6 (=CH, J = 160.5 Hz), 117.4 (C-5), 128.3, 128.5, 133.4, 136.3, 156.4, 158.6, 161.4, 177.0 (=COH).

Anal. Calcd. for $C_{15}H_{16}N_2O$ (240.3): C, 74.97; H, 6.71; N, 11.66. Found: C, 74.8; H, 6.9; N, 11.4.

X-Ray Crystal Structure Analysis of **4a** [26].

The data collection was carried out on an Enraf-Nonius CAD4 diffractometer. The structure was solved using direct methods (SHELXS-86) and refined on F^2 by a full-matrix least-squares method (SHELXL-93). Hydrogen atoms at N1 and N3 were located and refined, all other H atoms were included in calculated positions. Crystal and refinement data are given in Table 1, atomic coordinates in Table 2.

X-Ray Crystal Structure Analysis of **5a** [26].

Data collection was done on a Siemens P4 diffractometer. The structure was solved using direct methods (SHELXS-86), and refined on F^2 by a full-matrix least-squares method (SHELXL-93). Hydrogen atom positions were located in a difference Fourier map and refined. Crystal and refinement data are given in Table 1, atomic coordinates in Table 4.

REFERENCES AND NOTES

† Dedicated to Professor Richard Neidlein at the occasion of his 65th birthday.

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