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2-Azaallenium Salts from the Reaction of 1-Oxa-3-azabutatrienium Salts with Cyanamides and Carbodiimides

Mahmoud Al-Talib, Johannes C. Jochims, Laszlo Zsolnai,* and *Gottfried Huttner*

Fakultät für Chemie der Universität Konstanz,
Postfach 5560, D-7750 Konstanz

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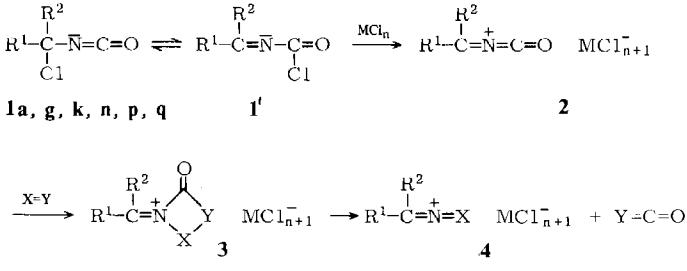
1-Oxa-3-azabutatrienium salts **2** react with disubstituted cyanamides under [2 + 2 + 2] cycloaddition affording the 2-(alkylideneamino)-4,6-diamino-1,3,5-oxadiazinium salts **7a – o**, which can be regarded as oxy-substituted 2-azaallenium salts. Addition of methanol leads to the oxadiazinium salts **8a, d, p**. From **2n** and dimethylcyanamide the 2-azaallenium salt **11** was obtained, which must be formed by an [1,5] isocyanatotropic rearrangement. Most butatrienium salts **2** react with two equivalents of carbodiimides $R^1-N=C=N-CHR_2^2$ to form the 2-azaallenium salts **17a – k**. The reaction mechanism includes an [1,5] hydride shift. Bulky substituted butatrienium salts **2** add three molecules of diisopropylcarbodiimide to give the 1,3,5-triazinium salts **20n, o**. *X*-Ray structural analyses for **7a** and **17a** are reported.

Darstellung von 2-Azaallenium-Salzen durch Reaktionen von 1-Oxa-3-azabutatrienium-Salzen mit Cyanamiden und Carbodiimiden

Die 1-Oxa-3-azabutatrienium-Salze **2** reagieren mit disubstituierten Cyanamiden unter [2 + 2 + 2]-Cycloaddition zu den 2-(Alkylidenamino)-4,6-diamino-1,3,5-oxadiazinium-Salzen **7a – o**, die man als oxysubstituierte 2-Azaallenium-Salze betrachten kann. Durch Anlagerung von Methanol entstehen die Oxadiazinium-Salze **8a, d, p**. Aus **2n** und Dimethylcyanamid erhält man das 2-Azaallenium-Salz **11**, dessen Bildung eine [1,5]-isocyanatotrope Umlagerung einschließt. Die Butatrienium-Salze **2** reagieren meist mit zwei Äquivalenten Carbodiimid vom Typ $R^1-N=C=N-CHR_2^2$ zu den 2-Azaallenium-Salzen **17a – k**, die durch eine [1,5]-Hydridverschiebung entstehen. Sterisch anspruchsvoll substituierte Butatrienium-Salze **2** lagern drei Moleküle Diisopropylcarbodiimid an und ergeben die 1,3,5-Triazinium-Salze **20n, o**. Es werden Röntgenstrukturanalysen der Verbindungen **7a** und **17a** angegeben.

α-Chloro isocyanates **1** or the tautomeric alkylidenecarbamoyl chlorides **1'**[1] react with Lewis acids MCl_n to give the heterocumulenes **2**, which according to an *X*-ray structural analysis are

Scheme 1



1a, g, k, n, p, q **1'** **2**

3 **4**

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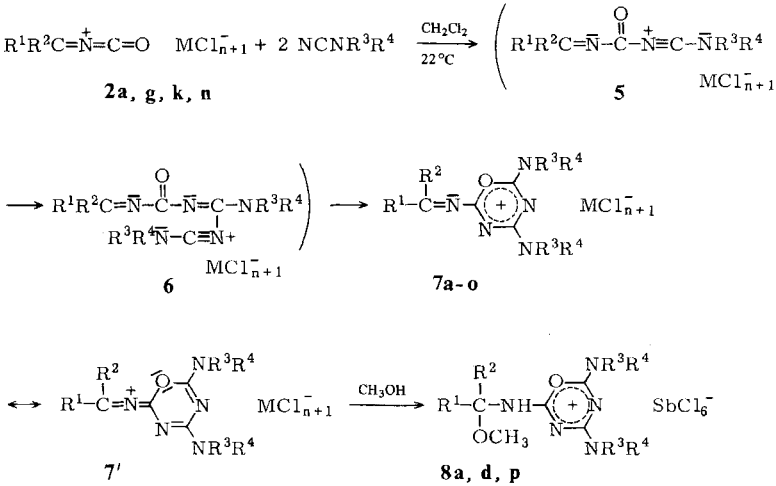
pseudocumulenes[2] with a C–N–C bond angle of about 130°[3]. The cations **2** undergo [2+2] cycloadditions and -reversions with double bonds according to Scheme 1.

With aldehydes, ketones, or tertiary carboxamides 2-azaallenium salts **4** (X = CR^3R^4, Y = O) are obtained[4]. Sulfoxides afford (alkylideneamino)sulfonium salts[2] (X = SR^3R^4, Y = O).

Reaction of 1-Oxa-3-azabutatrienium Salts with Disubstituted Cyanamides

In this paper [2+2+2] cycloadditions of the salts **2** with disubstituted cyanamides and carbodiimides are reported. Stirring a solution of **2a**, which was prepared in situ

Scheme 2



1, 2, 7, 8	R^1	R^2	R^3	R^4	MCl_{n+1}
a	C_6H_5	C_6H_5	CH_3	CH_3	$SbCl_6$
b	C_6H_5	C_6H_5	$-[CH_2]_5-$		$SbCl_6$
c	C_6H_5	C_6H_5	$CH(CH_3)_2$	CH_3	$SbCl_6$
d	C_6H_5	C_6H_5	$CH(CH_3)_2$	$CH(CH_3)_2$	$SbCl_6$
e	C_6H_5	C_6H_5	$CH(CH_3)_2$	$CH(CH_3)_2$	$FeCl_4$
f	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$SbCl_6$
g	2-C_6H_4–C_6H_4-2'		CH_3	CH_3	$SbCl_6$
h	2-C_6H_4–C_6H_4-2'		$-[CH_2]_5-$		$SbCl_6$
i	2-C_6H_4–C_6H_4-2'		$CH(CH_3)_2$	$CH(CH_3)_2$	$SbCl_6$
j	2-C_6H_4–C_6H_4-2'		$CH(CH_3)_2$	$CH(CH_3)_2$	$FeCl_4$
k	C_6H_5	1-$C_{10}H_7$	CH_3	CH_3	$SbCl_6$
l	C_6H_5	1-$C_{10}H_7$	$-[CH_2]_5-$		$SbCl_6$
m	C_6H_5	1-$C_{10}H_7$	$CH(CH_3)_2$	$CH(CH_3)_2$	$SbCl_6$
n	C_6H_5	$C(CH_3)_3$	$CH(CH_3)_2$	$CH(CH_3)_2$	$SbCl_6$
o	$C(CH_3)_3$	$C(CH_3)_3$	$CH(CH_3)_2$	$CH(CH_3)_2$	$SbCl_6$
p	C_6H_5	4-BrC_6H_4	CH_3	CH_3	$SbCl_6$

from **1a** and antimony pentachloride in dichloromethane at −78 °C, with two equivalents of dimethylcyanamide for two hours at room temperature afforded the 2-azaallenium salt **7a** in 98% yield. Similarly, compounds **7b – o** were prepared.

The structures of compounds **7** are elucidated by an *X*-ray diffraction analysis of **7a** and are based on the NMR spectra. In analogy to other oxadiazinium salts[5] signals at 162.1, 159.4, and 156.4 ppm (CD_2Cl_2, 263 K) in the ^{13}C NMR spectra of **7a** may be assigned to carbons of the heterocycle. A resonance at 182.2 ppm must be attributed to the diphenylmethylene carbon. At room temperature the methyl groups of **7a** give rise to four separate signals indicating considerable double bond character of the $C-N(CH_3)_2$ bonds. According to the ^{13}C NMR spectrum of **7a**, which shows only four resonances for the two phenyl groups between 200 and 300 K, there must be a plane of symmetry bisecting the $C_6H_5-C-C_6H_5$ angle. *X*-Ray diffraction analyses of many 2-azaallenium salts $R^1_2C=\overset{+}{N}=CR^2_2\ X^-$ have shown that these compounds have planes through R^1_2C and R^2_2C, which are more or less perpendicular with respect to each other[6–9].

Only a few 1,3,5-oxadiazinium salts are described in the literature. They can be prepared by cycloaddition of acylium salts to nitriles[10–15] or by alkylation of oxadiazinones[16]. Obviously, **2** behave as acylium salts in the reaction with cyanamides.

Compounds **7** are probably formed by stepwise polar cycloadditions[17,18] via nitrilium intermediates **5** and **6**. Four-membered cyclic intermediates of type **3**, for which a canonical form of an antiaromatic 1,3-diazacyclobutadiene may be written, seem unlikely.

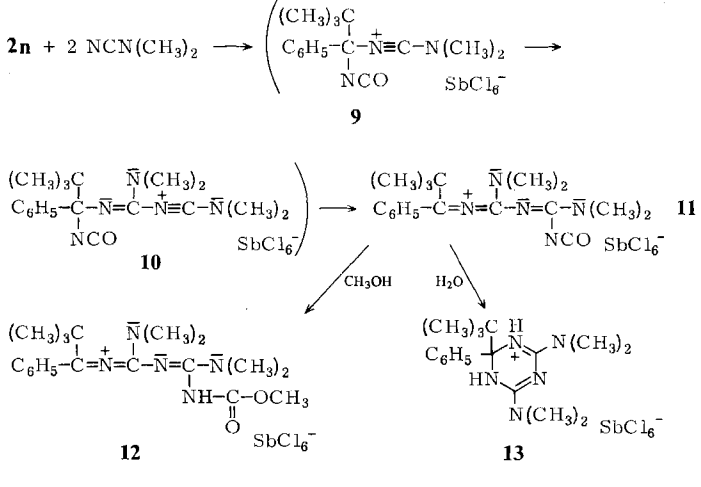
The cycloaddition is limited to electron-rich nitriles. No reaction was observed between **2a** and acetonitrile, phenyl cyanate, or isopropyl thiocyanate.

Recently, *Würthwein* et al.[19] prepared the first oxy-substituted 2-azaallenium salts.

Compounds **7** are only moderately reactive against nucleophiles, e.g. **7e** can be precipitated unchanged from its solution in methanol/dichloromethane with ether. Only after prolonged treatment with methanol the methoxy compounds **8** are obtained.

While the *tert*-butyl-substituted **2n** reacted with diisopropylcyanamide in the expected way to give the oxadiazinium salt **7n**, the reaction took a different course with dimethylcyanamide. With this sterically less demanding cyanamide the isocyanate **11** was obtained in 85% yield (IR (CH_2Cl_2): NCO 2240 cm^{-1}). The structure of **11** was sup-

Scheme 3



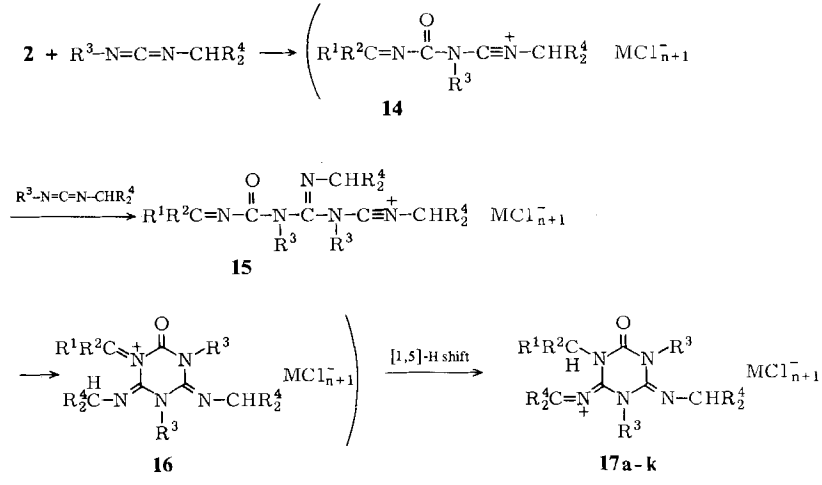
ported by its transformation to **12** with methanol. Hydrolysis of **11** leads to the *s*-triazinium salt **13**.

In alkyl-substituted butatrienium salts **2** the positive charge α to the isocyanato group can not as effectively be dissipated into the substituents as in diaryl-substituted salts **2**. Therefore, sterically unpretentious nucleophiles like dimethylcyanamide attack **2n** at the α-position to the isocyanato group while the more encumbering diisopropylcyanamide adds to the isocyanato carbon of the ambident electrophile **2n**. The isocyanatotropic [1,5] shift **10** ↔ **11** could well proceed in a concerted suprafacial way[1].

Reaction of 1-Oxa-3-azabutatrienium Salts with Carbodiimides

A new type of triazinium salts was obtained from the reaction of **2** with aliphatic carbodiimides. From the reaction mixture of **2a** with two equivalents of diisopropylcarbodiimide in dichloromethane at room temperature the 2-azaallenium salt **17a** was isolated in an almost quantitative yield. Similarly, compounds **17b – k** were prepared.

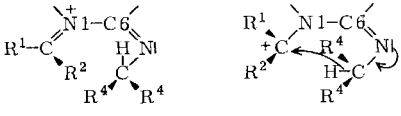
Scheme 4



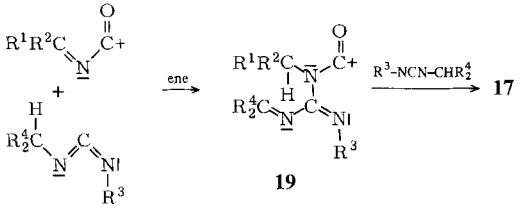
17	R^1	R^2	R^3	R^4	R^4	MCl_{n+1}
a	C_6H_5	C_6H_5	$CH(CH_3)_2$	CH_3	CH_3	$SbCl_6$
b	C_6H_5	C_6H_5	$CH(CH_3)_2$	CH_3	CH_3	$FeCl_4$
c	C_6H_5	C_6H_5	$CH(CH_3)_2$	CH_3	CH_3	$ZnCl_3$
d	C_6H_5	C_6H_5	$c\text{-}C_6H_{11}$	$-[CH_2]_5-$		$SbCl_6$
e	C_6H_5	C_6H_5	$c\text{-}C_6H_{11}$	$-[CH_2]_5-$		$FeCl_4$
f	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$		$CH(CH_3)_2$	CH_3	CH_3	$SbCl_6$
g	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$		$CH(CH_3)_2$	CH_3	CH_3	$FeCl_4$
h	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$		$CH(CH_3)_2$	CH_3	CH_3	$ZnCl_3$
i	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$		$c\text{-}C_6H_{11}$	$-[CH_2]_5-$		$SbCl_6$
j	C_6H_5	$1\text{-}C_{10}H_7$	$CH(CH_3)_2$	CH_3	CH_3	$SbCl_6$
k	C_6H_5	$1\text{-}C_{10}H_7$	$c\text{-}C_6H_{11}$	$-[CH_2]_5-$		$SbCl_6$

At least three different mechanisms may be invoked to account for the formation of **17**. An intermediate **16**, formed via nitrilium precursors **14** and **15**, could rearrange by a fast pericyclic [1,5] sigmatropic hydrogen shift to give **17**. But, such a sigmatropic shift would require a conformation **18'**, in which R^2 and one of the substituents R^4 would come very close. Therefore, a direct hydride shift in a less crowded conformation **18''** seems to be more reasonable. Related [1,5] hydride shifts have recently been observed[20-22] in a reaction leading to the formation of cyclopentenones via alkyne acylation. Finally, **17** may be formed by an ene reaction of **2** with one mol of carbodiimide yielding an intermediate **19**, which cyclizes in a concerted or stepwise [4 + 2] addition of a second mol of carbodiimide. Ene reactions of acylium cations with olefins containing an allylic hydrogen have, for instance, been observed by *Hoffmann* et al.[23]. Although the direct hydride shift from **18''** seems most plausible, other mechanisms cannot be ruled out at time.

The constitution of compound **17a** has been confirmed by an *X*-ray structural analysis.



18' **18''**



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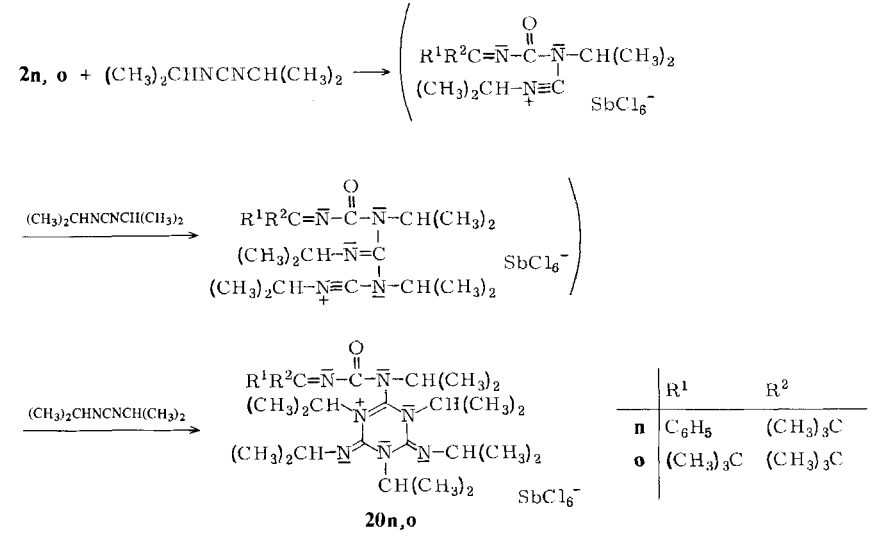
Reaction of Bulky Substituted 1-Oxa-3-azabutatrienium Salts with Carbodiimides



	R^1	R^2
n	C_6H_5	$(CH_3)_3C$
o	$(CH_3)_3C$	$(CH_3)_3C$

20n,o

Still another type of triazinium salts was obtained from the reaction of bulky substituted butatrienium salts **2** with aliphatic carbodiimides. Under conditions where **2k** reacts with two equivalents of diisopropylcarbodiimides to give **17j** the *tert*-butyl-substituted cumulenes **2n, o** consume three equivalents of carbodiimide affording the triazinium hexachloroantimonates **20n, o** in moderate yields. At 303 K the ^{13}C and ^{1}H NMR spectra of **20** show six inequivalent isopropyl groups indicating coplanarity of the carbamoyl moiety and the triazinium ring. For both compounds **20** signals for only one *tert*-butyl group are observed. Therefore, at room temperature the rotation around the C=N double bonds with the *tert*-butyl substituents must be fast on the NMR time scale.

X-Ray Diffraction Analyses for 7a and 17a*)

7a, $[C_{20}H_{22}N_5O]^+[SbCl_6]^-$, orthorhombic, space group $P2_12_12_1$ (No. 19[24]), $Z = 4$, $a = 965$ (1), $b = 1473$ (2), $c = 1913$ (3) pm, $V = 2718 \cdot 10^6$ pm^3, $d_{calc.} = 1.6$ gcm^{-3}, $\mu_{Mo\text{-}K_\alpha} = 16.3$ cm^{-1}, $T = 213$ K, ω-scan, $\Delta\omega = 1°$, $2.2 \leqslant \dot{\omega} \leqslant 29.3°$ min^{-1}, $1° \leqslant 2\theta \leqslant 44°$, 1783 independent significant reflections ($I \geqslant 2\sigma$).

17a, $[C_{28}H_{38}N_5O]^+[SbCl_6]^- \cdot CH_2Cl_2$, monoclinic, space group $P2_1/c$ (No. 14[24]), $Z = 4$, $a = 890.0$ (7), $b = 1504$ (2), $c = 2922$ (4) pm, $\beta = 92.52$ (9)°, $d_{calc.} = 1.5$ gcm^{-3}, $\mu_{Mo\text{-}K_\alpha} = 12.9$ cm^{-1}, $T = 238$ K, ω-scan, $\Delta\omega = 1.0°$, $2.2 \leqslant \dot{\omega} \leqslant 29.3°$ min^{-1}, $2° \leqslant 2\theta \leqslant 42°$, 3288 independent significant reflections ($I \geqslant 2\sigma$).

Table 1. Fractional Atomic Coordinates and Temperature Parameters for **7a**[a]

atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb	0.67038(6)	0.68282(4)	0.20109(3)	0.0290(3)	0.0247(3)	0.0314(3)	0.0014(3)	-0.0034(3)	-0.0009(3)
Cl1	0.5205(2)	0.8101(2)	0.1970(2)	0.040(1)	0.052(1)	0.069(2)	0.003(2)	-0.007(2)	0.018(1)
Cl2	0.8237(3)	0.5586(1)	0.2050(2)	0.069(2)	0.029(1)	0.062(2)	0.007(1)	-0.001(2)	0.016(1)
Cl3	0.7961(2)	0.7541(2)	0.2913(1)	0.039(1)	0.052(1)	0.050(2)	-0.017(1)	-0.012(1)	0.002(1)
Cl4	0.5453(3)	0.6149(2)	0.1091(1)	0.062(2)	0.071(2)	0.056(2)	-0.017(2)	-0.018(2)	-0.014(2)
Cl5	0.8200(3)	0.7529(2)	0.1189(1)	0.045(1)	0.046(1)	0.053(1)	0.020(1)	0.010(1)	0.002(2)
Cl6	0.5270(3)	0.6142(2)	0.2847(2)	0.055(2)	0.077(2)	0.060(2)	0.018(2)	0.013(2)	-0.022(2)
O	0.8572(7)	0.3339(4)	0.2538(3)	0.052(4)	0.021(3)	0.021(3)	0.001(3)	0.006(3)	0.001(3)
N1	0.8265(7)	0.1921(4)	0.3047(3)	0.038(4)	0.019(3)	0.024(3)	0.006(3)	-0.004(4)	-0.003(4)
N2	0.8598(7)	0.2072(4)	0.1804(3)	0.027(4)	0.028(4)	0.020(3)	0.002(3)	-0.005(3)	0.002(3)
N3	0.8246(8)	0.3225(5)	0.3687(3)	0.042(4)	0.028(4)	0.019(3)	0.000(3)	0.008(4)	-0.004(5)
N4	0.9316(7)	0.3523(4)	0.1449(3)	0.032(4)	0.022(4)	0.021(4)	0.002(3)	0.006(3)	-0.003(3)
N5	0.8139(9)	0.0687(4)	0.2314(4)	0.055(5)	0.016(4)	0.037(4)	0.002(3)	-0.002(4)	0.001(4)

atom	x/a	y/b	z/c	U	atom	x/a	y/b	z/c	U
C1	0.8352(9)	0.2793(5)	0.3099(4)	0.026(2)	C2	0.832(1)	0.1576(5)	0.2404(4)	0.027(2)
C3	0.8759(8)	0.2933(5)	0.1907(4)	0.028(2)	C4	0.8802(8)	0.3839(5)	0.0879(4)	0.022(2)
C5	0.9769(8)	0.4427(5)	0.0474(4)	0.023(2)	C6	1.1169(9)	0.4266(6)	0.0487(4)	0.029(2)
C7	1.209(1)	0.4856(7)	0.0162(5)	0.041(3)	C8	1.156(1)	0.5623(6)	-0.0173(5)	0.040(2)
C9	1.017(1)	0.5780(7)	-0.0180(5)	0.048(3)	C10	0.923(1)	0.5201(6)	0.0148(5)	0.038(2)
C11	0.7391(9)	0.3657(6)	0.0614(4)	0.026(2)	C12	0.7150(9)	0.3552(6)	-0.0096(5)	0.032(2)
C13	0.5854(9)	0.3352(6)	-0.0350(5)	0.038(2)	C14	0.478(1)	0.3223(7)	0.0105(5)	0.043(2)
C15	0.497(1)	0.3331(7)	0.0810(5)	0.043(3)	C16	0.6277(9)	0.3537(6)	0.1072(4)	0.031(2)
C17	0.830(1)	0.4217(7)	0.3746(5)	0.053(3)	C18	0.802(1)	0.2709(6)	0.4329(5)	0.042(3)
C19	0.807(1)	0.0274(7)	0.1626(5)	0.047(3)	C20	0.787(1)	0.0102(6)	0.2907(5)	0.045(3)

a) The anisotropic thermal parameters are defined by the equation: $T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$.

*) Further details and basic data concerning the *X*-ray analyses may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying the registry number CSD 50870, authors, and source.

Table 2. Fractional Atomic Coordinates and Temperature Parameters for **17a** (Definition of *U* see Table 1)

atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb	0.0945(1)	0.31585(5)	0.27700(3)	0.0481(5)	0.0259(4)	0.0348(5)	0.0026(4)	-0.0063(4)	-0.0043(4)
Cl1	0.1183(4)	0.3004(2)	0.1966(1)	0.083(3)	0.057(2)	0.038(2)	0.001(2)	0.004(2)	-0.026(2)
Cl2	0.0683(4)	0.3335(3)	0.3564(1)	0.089(3)	0.068(2)	0.034(2)	0.000(2)	-0.006(2)	0.015(2)
Cl3	0.0460(5)	0.1622(2)	0.2815(1)	0.107(3)	0.028(2)	0.071(2)	0.012(2)	0.013(2)	-0.006(2)
Cl4	-0.1682(4)	0.3405(3)	0.2662(1)	0.050(2)	0.075(3)	0.063(2)	0.000(2)	-0.015(2)	0.011(2)
Cl5	0.3547(4)	0.2866(3)	0.2890(1)	0.053(2)	0.102(3)	0.084(3)	-0.025(3)	-0.015(2)	0.017(2)
Cl6	0.1441(5)	0.4680(2)	0.2692(2)	0.117(4)	0.030(2)	0.087(3)	-0.006(2)	0.017(3)	-0.022(2)
N2	0.499(1)	0.2138(6)	0.1446(3)	0.040(6)	0.026(5)	0.043(6)	0.006(4)	-0.015(5)	0.001(5)
N3	0.502(1)	0.0714(6)	0.1175(4)	0.081(9)	0.027(6)	0.060(7)	-0.001(5)	-0.007(6)	-0.004(6)
N4	0.3836(9)	0.3083(6)	0.0907(3)	0.022(5)	0.027(5)	0.034(5)	0.003(4)	-0.003(4)	-0.011(4)
N5	0.598(1)	0.3565(6)	0.1329(3)	0.033(6)	0.031(5)	0.038(6)	0.007(5)	-0.006(5)	-0.002(5)
N6	0.280(1)	0.1672(6)	0.1023(3)	0.039(6)	0.028(6)	0.064(7)	0.012(5)	-0.013(5)	-0.025(5)
O	0.1357(8)	0.2804(5)	0.0717(3)	0.023(5)	0.044(5)	0.060(6)	0.009(4)	-0.005(4)	-0.009(4)
ClX1	0.2304(6)	0.6957(5)	-0.0403(2)	0.082(4)	0.214(7)	0.106(4)	-0.007(4)	0.011(3)	0.053(4)
ClX2	0.1812(9)	0.8205(4)	0.0330(2)	0.241(8)	0.096(4)	0.165(6)	-0.049(4)	-0.077(6)	0.004(5)

atom	x/a	y/b	z/c	U	atom	x/a	y/b	z/c	U
C1	0.424(1)	0.1423(8)	0.1195(4)	0.039(3)	C3	0.489(1)	0.2945(7)	0.1248(4)	0.030(3)
C5	0.254(1)	0.2526(8)	0.0872(4)	0.038(3)	C61	0.124(2)	0.115(1)	0.1128(6)	0.087(5)
C62	0.082(2)	0.070(2)	0.0665(7)	0.119(7)	C63	0.147(2)	0.063(2)	0.1566(7)	0.122(7)
C31	0.462(2)	-0.006(1)	0.0887(5)	0.078(5)	C32	0.592(3)	-0.013(2)	0.0562(8)	0.127(7)
C33	0.465(2)	-0.088(1)	0.1201(6)	0.083(5)	C8	0.351(1)	0.3043(8)	-0.0108(4)	0.040(3)
C9	0.315(1)	0.3788(7)	0.0156(4)	0.033(3)	C10	0.214(1)	0.4421(7)	-0.0032(4)	0.035(3)
C11	0.147(1)	0.4300(8)	-0.0470(4)	0.048(3)	C12	0.181(1)	0.3546(8)	-0.0730(4)	0.047(3)
C13	0.284(1)	0.2915(8)	-0.0541(4)	0.046(3)	C14	0.392(1)	0.3929(7)	0.0627(3)	0.028(3)
C15	0.338(1)	0.4743(7)	0.0885(4)	0.029(3)	C16	0.207(1)	0.4731(8)	0.1133(4)	0.039(3)
C17	0.165(1)	0.5494(8)	0.1376(4)	0.047(3)	C18	0.252(2)	0.6269(9)	0.1361(4)	0.053(4)
C19	0.383(2)	0.6276(9)	0.1109(4)	0.054(4)	C20	0.427(1)	0.5511(8)	0.0868(4)	0.039(3)
C51	0.607(1)	0.4178(8)	0.1637(4)	0.038(3)	C52	0.495(1)	0.4335(9)	0.1990(4)	0.050(3)
C53	0.745(2)	0.4779(9)	0.1625(5)	0.057(4)	C21	0.611(1)	0.1978(8)	0.1851(4)	0.046(3)
C22	0.765(2)	0.174(1)	0.1679(5)	0.062(4)	C23	0.544(2)	0.1278(9)	0.2174(5)	0.061(4)
CX1	0.135(2)	0.721(1)	0.0076(5)	0.074(4)					

Table 3. Selected Bond Angles and Torsional Angles [°] for **7a** and **17a**

7a	C4 - N4 - C3	129.2(8)	C1 - O - C3	117.5(6)	C3 - N2 - C2 - N5	+179.6(8)
	C5 - C4 - N4	114.2(7)	C1 - N3 - C17	123.6(7)	N1 - C2 - N5 - C20	+ 1(1)
	C11 - C4 - N4	125.6(7)	C1 - N3 - C18	119.0(7)	N2 - C2 - N5 - C20	+178.7(8)
	C5 - C4 - C11	120.2(7)	C17 - N3 - C18	117.3(7)	N2 - C2 - N1 - C1	+ 7(1)
	N4 - C3 - N2	125.5(8)	C5 - C4 - N4 - C3	-175.3(8)	C2 - N1 - C1 - N3	+176.4(9)
	N4 - C3 - O	110.3(7)	C11 - C4 - N4 - C3	+ 4(1)	C2 - N1 - C1 - O	- 4(1)
	C3 - N2 - C2	114.4(7)	C4 - N4 - C3 - N2	+ 73(1)	N1 - C1 - O - C3	- 3(1)
	N2 - C2 - N1	124.8(7)	C4 - N4 - C3 - O	-116.5(9)	N1 - C1 - N3 - C17	-177.9(9)
	N2 - C2 - N5	115.9(7)	C6 - C5 - C4 - N4	+ 32(1)	N1 - C1 - N3 - C18	0(1)
	C2 - N1 - C1	116.7(7)	C12 - C11 - C4 - N4	-143.0(9)	C1 - O - C3 - N4	-163.9(7)
	C2 - N5 - C19	122.3(7)	C6 - C5 - C4 - C11	-147.4(8)	C1 - O - C3 - N2	+ 7(1)
	C2 - N5 - C20	120.4(7)	C12 - C11 - C4 - C5	+ 37(1)	C1 - N1 - C2 - N5	-175.5(9)
	C19 - N5 - C20	117.0(7)	N4 - C3 - N2 - C2	+165.1(8)	N3 - C1 - O - C3	+177.0(8)
	N1 - C1 - O	122.6(7)	N4 - C3 - O - C1	-163.9(7)	O - C3 - N2 - C2	- 5(1)
	N1 - C1 - N3	123.4(7)	C3 - N2 - C2 - N1	- 3(1)	O - C1 - N3 - C17	+ 3(1)
17a	C3 - N5 - C51	129(1)	N6 - C1 - N3	134(1)	N2 - C1 - N6 - C5	+ 36(1)
	N5 - C51 - C52	125(1)	C1 - N2 - C21	123.0(9)	N2 - C1 - N6 - C61	-124(1)
	N5 - C51 - C53	116(1)	N4 - C14 - C9	109.8(8)	C1 - N3 - C31 - C32	+118(2)
	C52 - C51 - C53	119(1)	N4 - C14 - C15	112.3(8)	C1 - N6 - C5 - O	+180(1)
	N4 - C3 - N2	118.9(9)	C9 - C14 - C15	114.5(8)	C1 - N6 - C5 - N4	+ 1(2)
	C3 - N2 - C1	115.6(9)	N4 - C3 - N5 - C51	+100(1)	C1 - N6 - C61 - C62	-108(2)
	N2 - C1 - N6	112.1(9)	N2 - C3 - N5 - C51	- 92(1)	N6 - C5 - N4 - C3	- 31(1)
	C1 - N6 - C5	120.2(9)	C3 - N5 - C51 - C52	+ 1(2)	N6 - C5 - N4 - C14	+160.2(9)
	N6 - C5 - N4	113.5(9)	N4 - C3 - N2 - C21	-176.2(9)	O - C5 - N4 - C14	- 19(2)
	N6 - C5 - O	126(1)	C3 - N2 - C21 - C22	- 86(1)	C5 - N4 - C3 - N2	+ 23(1)
	O - C5 - N4	121(1)	N4 - C3 - N2 - C1	+ 16(1)	C5 - N4 - C3 - N5	-168.5(9)
	C5 - N4 - C3	119.8(9)	N5 - C3 - N2 - C1	-152(1)	C5 - N4 - C14 - C9	- 36(1)
	N4 - C3 - N5	119.2(9)	C3 - N2 - C1 - N6	- 44(1)	C5 - N4 - C14 - C15	+ 93(1)
	C5 - N4 - C14	120.9(8)	C3 - N2 - C1 - N3	+135(1)	N4 - C14 - C9 - C8	- 50(1)
	C5 - N6 - C61	112(1)	N2 - C1 - N3 - C31	-171(1)	N4 - C14 - C15 - C16	- 44(1)

The cell constants and the intensities were determined on a Syntex P3-diffractometer (graphite monochromator, $\lambda_{Mo\text{-}K_\alpha}$ = 71.069 pm). The structures were solved by the Patterson heavy-atom method using the program SHEL-XTL[25]. Atomic form factors of neutral atoms were used. Partial anisotropic full-matrix least-squares refinement led to agreement factors R_1 = 0.032 and R_2 = 0.035 for **7a** as well as R_1 = 0.067 and R_2 = 0.073 for **17a**.

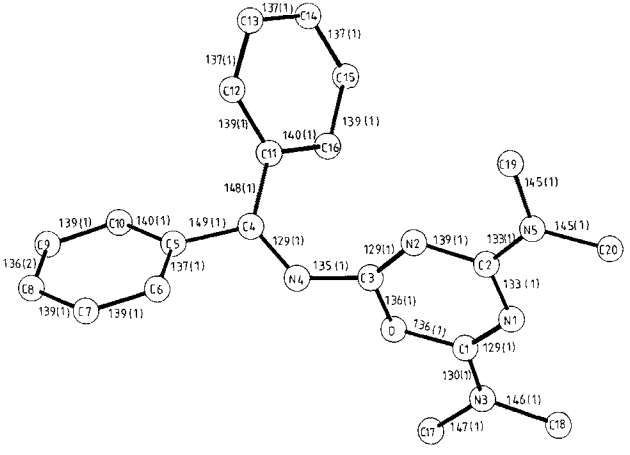


Fig. 1. Molecular Drawing and Bond Lengths [pm] for the Cation of **7a**

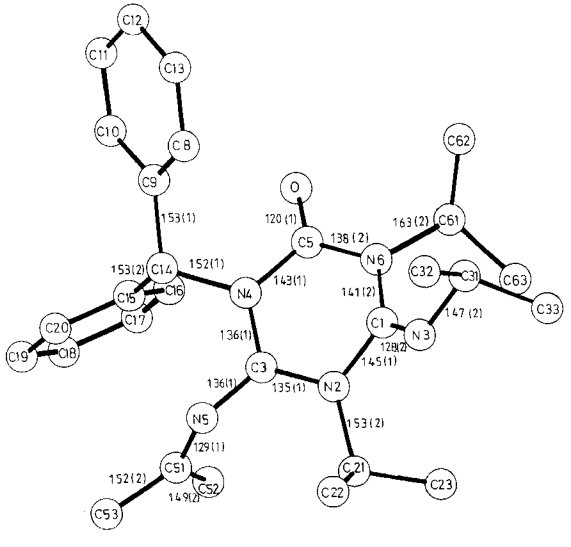
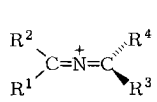


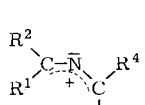
Fig. 2. Molecular Drawing and Selected Bond Lengths [pm] for the Cation of **17a**

Lists of atomic coordinates with LS-computed standard deviations are given in Tables 1 and 2. In Table 3 selected bond angles and torsional angles for both compounds are listed. Fig. 1 and 2 show drawings of the cations of **7a** and **17a**.

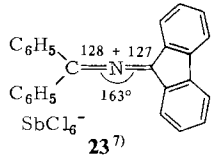
The structural proposals for **7a** and **17a** are confirmed by the *X*-ray results. The molecules consist of discrete $[C_{20}H_{22}N_5O]^+$ or $[C_{28}H_{38}N_5O]^+$ cations, resp., and $SbCl_6^-$ anions. For 2-azaallenium cations qualitative valence bond arguments suggest two valence tautomeric structures **21** or **22** with local D_{2d} and C_{2v} symmetry, respectively. Recent *ab initio* calculations[7] predict a planar 2-azaallylium structure **22** for the 1,1-diamino-2-azaallenium cation ($R^1 = R^2 = NH_2$, $R^3 = R^4 = H$). In accordance with results for other 2-azaallenium salts[6-9] the *X*-ray data for **7a** and **17a** show that neither valence bond structure (**21**, **22**) satisfactorily represents the real molecules. In both compounds the 2-azaallenium units are bent (**7a**: C4 – N4 – C3 129.2 (8)°, **17a**: C3 – N5 – C51 129 (1)°) and show unequal C = N bond lengths. The coplanarity of C5, C4, C11, N4, C3 in **7a** and C53, C51, C52, N5, C3 in **17a** together with the short distances C4 – N4 in **7a** and C51 – N5 in **17a** (both 129 (1) pm) suggest that these compounds are azomethines rather than 2-azaallenium salts. For comparison, *X*-ray diffraction data for the 2-azaallenium cation **23**[7] and *N*-benzylideneaniline (**24**)[26] are shown (bond lengths in pm). In both **7a** and **17a** the heterocyclic ring is not completely planar. But the large torsional angles C4 – N4 – C3 – N2 73 (1)° for **7a** and N4 – C3 – N5 – C51 100 (1)° for **17a** indicate that the planes through the end groups (C5, C4, C11 and C3, O, N2 in **7a**, C53, C51, C52 and N4, C3, N2 in **17a**)of the 2-azaallenium moieties are almost perpendicular with respect to each other. For **23** the corresponding torsional angle was found to be 58°[7]. Similar results have been reported for 2-oxaallenium dications[27-29].



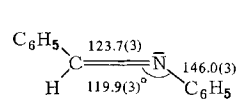
21 (D_{2d})



22 (C_{2v})



23[7]



24[26]

The positive charge of the cation **7a** is mainly delocalized over the polymethine unit N3 – C1 – N1 – C2 – N5. This is indicated by the coplanarity of these atoms with the carbons of the four methyl groups and by the short bond lengths C1 – N3 (130 (1) pm) and C2 – N5 (133 (1) pm). The positive charge of the cation **17a** is delocalized over the guanidinium unit N4 – C3 – N5 – N2. The C1 – N3 bond (128 (2) pm) is essentially a double bond, while N2 – C1 (145 (1) pm), C1 – N6 (141 (2) pm), and N4 – C5 (143 (1) pm) are single bonds. The shorter C5 – N6 distance (138 (2) pm) indicates charge delocalization within an amide group. The triazinium ring is far from being planar, C3 and N2 lying below the plane through C1 – N6 – C5 – N4.

M.A.-T. would like to thank *Yarmouk University, Jordan,* for a study leave and *Deutscher Akademischer Austauschdienst* for a scholarship. We would like to thank Mr. *S. Herzberger* for technical assistance.

Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer, solutions in dichloromethane. – ^1H NMR spectra: JEOL JNM-MH-100 and Bruker WM-250 instruments. – ^{13}C NMR spectra: Bruker WM-250 spectrometer; δ-scale; internal reference tetramethylsilane. – The melting points are uncorrected.

2,4-Bis(dimethylamino)-6-[(diphenylmethylene)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**7a**): To **1a**[30] (1.22 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) was added dropwise with stirring at −78 °C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) and then a solution of dimethylcyanamide (0.71 g, 10.13 mmol). The reaction mixture was stirred for 2 h at 22 °C. Slow addition of anhydrous pentane (50 ml) afforded a yellow precipitate, which was recrystallized from dichloromethane/pentane. Yield 3.34 g (98%) of yellow needles; m.p. 152–155 °C. – IR: 1700, 1630, 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2, 303 K): CH_3 δ = 3.10, 3.11, 3.26, 3.27. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 36.9, 38.0, 38.2, 38.3, phenyl: *ipso,p*-C 135.1, 133.8, *o,m*-C 130.5, 129.3, C=N, C=O 182.2, 162.1, 159.5, 156.4.

$[C_{20}H_{22}N_5O]SbCl_6$ (682.9) Calcd. C 35.17 H 3.25 N 10.26 Found C 34.85 H 3.17 N 10.12

2-[(Diphenylmethylene)amino]-4,6-dipiperidino-1,3,5-oxadiazinium Hexachloroantimonate (**7b**): From 1-piperidinecarbonitrile[31] (1.11 g, 10.08 mmol) as described for **7a**. At −25 °C with anhydrous ether (50 ml) a yellow powder was precipitated. Recrystallization from dichloromethane/ether afforded yellow prisms (3.43 g, 90%); m.p. 182–184 °C. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_2N δ = 45.9, 46.7, 47.0, CH_2 23.7, 24.1, 25.4, 25.8, 26.1, phenyl: *ipso,p*-C 135.2, 133.7, *o,m*-C 130.5, 129.2, C=O, C=N 182.4, 162.5, 157.8, 155.1.

$[C_{26}H_{30}N_5O]SbCl_6$ (763.0) Calcd. C 40.92 H 3.96 N 9.18 Found C 40.75 H 3.74 N 9.09

2-[(Diphenylmethylene)amino]-4,6-bis(isopropylmethylamino)-1,3,5-oxadiazinium Hexachloroantimonate (**7c**): From isopropylmethylcyanamide[32] (0.99 g, 10.09 mmol) as described for **7b**. Recrystallization from dichloromethane (10 ml)/ether (50 ml) afforded a yellow powder (3.25 g, 88%); m.p. 92–100 °C (dec.). – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 19.1, 19.6, 19.7, 19.9, NCH_3 28.5, 29.8, 29.9, CHN 49.5, 49.7, 49.9, 50.4, C=O, C=N 182.4, 182.3, 162.5, 162.4, 158.9, 156.1, 155.9, 8 aromatic C.

$[C_{24}H_{30}N_5O]SbCl_6$ (739.0) Calcd. C 39.00 H 4.09 N 9.48 Found C 38.95 H 4.09 N 9.39

2,4-Bis(diisopropylamino)-6-[(diphenylmethylene)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**7d**): From diisopropylcyanamide (1.27 g, 10.06 mmol) as described for **7a**. Yield 3.54 g (89%) of pale yellow needles; m.p. 179 °C. – ^1H NMR (CD_2Cl_2, 303 K): CH_3 δ = 1.10 (d, *J* = 7 Hz), 1.32 (d, *J* = 7 Hz), 1.37 (12H, d, *J* = 7 Hz). – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 19.8, 20.1, 20.8, 21.1, CHN 48.8, 49.7, 50.1, 50.5, phenyl: *ipso,p*-C 135.4, 133.9, *o,m*-C 130.5, 129.5, C=O, C=N 181.4, 161.6, 158.6, 155.9.

$[C_{28}H_{38}N_5O]SbCl_6$ (795.1) Calcd. C 42.29 H 4.82 N 8.81 Found C 41.94 H 4.74 N 8.67

2,4-Bis(diisopropylamino)-6-[(diphenylmethylene)amino]-1,3,5-oxadiazinium Tetrachloroferrate (**7e**): In analogy to **7d** with anhydrous $FeCl_3$ (0.81 g, 5.00 mmol), instead of $SbCl_5$. After 2 h stirring at 22 °C the solvent was evaporated under reduced pressure. The residue was stirred for 30 min in a mixture of anhydrous dichloromethane (10 ml)/methanol (10 ml). Slow addition of anhydrous ether (50 ml) afforded green-yellow needles (2.01 g, 61%); m.p. 283–287 °C. – IR: 1680, 1560 cm^{-1}.

$[C_{28}H_{38}N_5O]FeCl_4$ (658.3) Calcd. C 51.08 H 5.82 N 10.64 Found C 50.83 H 5.84 N 10.53

2,4-Bis(diphenylamino)-6-[(diphenylmethylene)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**7f**): From diphenylcyanamide[33] (1.95 g, 10.04 mmol) as described for **7a**, but without recrystallization. Yield 4.09 g (86%) of a pale yellow powder; m.p. 208–210 °C. – ^{13}C NMR (CD_2Cl_2, 263 K): C=O, C=N δ = 183.0, 163.1, 161.1, 157.4.

$[C_{40}H_{30}N_5O]SbCl_6$ (931.2) Calcd. C 51.59 H 3.25 N 7.52 Found C 51.51 H 3.16 N 7.24

2,4-Bis(dimethylamino)-6-(9-fluorenylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (**7g**): From **1g**[7] (1.21 g, 5.00 mmol) and dimethylcyanamide (0.71 g, 10.13 mmol) as described

for **7b**. Yield 2.86 g (84%), orange needles; m.p. 199–203 °C. – IR: 1710, 1670, 1625 (shoulder 1590) cm^{-1}. – ^1H NMR (CD_3CN/CD_2Cl_2 2:1, 263 K): CH_3 δ = 37.0, 38.1, 38.2, 38.4, C=O, C=N 172.6, 162.3, 159.5, 156.8.

$[C_{20}H_{20}N_5O]SbCl_6$ (680.9) Calcd. C 35.28 H 2.96 N 10.29 Found C 35.04 H 2.86 N 10.07

2-(9-Fluorenylideneamino)-4,6-dipiperidino-1,3,5-oxadiazinium Hexachloroantimonate (**7h**): From **1g** (1.21 g, 5.00 mmol) and 1-piperidinecarbonitrile (1.11 g, 10.08 mmol) as described for **7a**. Yield 3.42 g (90%) of orange needles; m.p. 132–134 °C. – ^{13}C NMR (CD_2Cl_2, 303 K): CH_2 δ = 22.6, 23.8, 24.2, 25.8, 26.1, NCH_2 46.2, 47.1, 47.3, 47.5, aromatic C 121.6, 126.9, 129.7, 133.0, 136.4, 144.6, C=O, C=N 173.1, 162.2, 158.1, 155.5.

$[C_{26}H_{28}N_5O]SbCl_6$ (761.0) Calcd. C 41.03 H 3.71 N 9.21 Found C 40.49 H 3.98 N 9.14

2,4-Bis(diisopropylamino)-6-(9-fluorenylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (**7i**): From **1g** (1.21 g, 5.00 mmol) and diisopropylcyanamide (1.27 g, 10.06 mmol) as described for **7b**. Yield 3.17 g (80%) of an orange powder; m.p. 242–244 °C (dec.). – IR: 1690, 1660, 1580 (shoulder 1560) cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 19.9, 20.3, 21.1, 21.3, CH 49.0, 50.0, 50.4, 50.8, aryl C 121.8, 126.7, 129.7, 133.0, 136.5, 144.7, C=O, C=N 172.6, 161.1, 158.5, 156.0.

$[C_{28}H_{36}N_5O]SbCl_6$ (793.1) Calcd. C 42.40 H 4.58 N 8.83 Found C 42.26 H 4.45 N 8.71

2,4-Bis(diisopropylamino)-6-(9-fluorenylideneamino)-1,3,5-oxadiazinium Tetrachloroferrate (**7j**): As described for **7a** from **1g** (1.21 g, 5.00 mmol), diisopropylcyanamide (1.27 g, 10.06 mmol), and anhydrous $FeCl_3$ (0.81 g, 5.00 mmol). The product was precipitated from the reaction mixture with pentane (80 ml). Yield 2.72 g (83%) of brown-yellow crystals; m.p. 198–201 °C (dec.). – IR: 1690, 1660, 1580, 1550 cm^{-1}.

$[C_{28}H_{36}N_5O]FeCl_4$ (656.3) Calcd. C 51.24 H 5.53 N 10.67 Found C 51.36 H 5.50 N 10.60

2,4-Bis(dimethylamino)-6-[(1-naphthylphenylmethylene)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**7k**): From **1k**[30] (1.47 g, 5.00 mmol) and dimethylcyanamide (0.71 g, 10.13 mmol) as described for **7a**. Recrystallization from dichloromethane (3 ml)/pentane (2 ml) at –25 °C afforded a yellow powder (2.49 g, 68%); m.p. 69–70 °C. – IR: 1700, 1630, 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2, 303 K): CH_3 δ = 2.79, 3.03, 3.13, 3.17. – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 36.9, 37.9, 38.2, 38.3, C=O, C=N 182.6, 162.3, 159.3, 156.5.

$[C_{24}H_{24}N_5O]SbCl_6$ (733.0) Calcd. C 39.33 H 3.30 N 9.56 Found C 39.19 H 3.39 N 9.51

2-[(1-Naphthylphenylmethylene)amino]-4,6-dipiperidino-1,3,5-oxadiazinium Hexachloroantimonate (**7l**): From 1-piperidinecarbonitrile (1.11 g, 10.08 mmol) as described for **7k**. Recrystallizations from dichloromethane (5 ml)/pentane (2 ml) at –25 °C, and from dichloromethane/pentane/ether afforded yellow crystals (2.32 g, 57%); m.p. 114–117 °C. – IR: 1680, 1610, 1570 cm^{-1}. – ^1H NMR (CD_3CN, 263 K): NCH_2 δ = 3.20 (m), 3.48 (m), 3.64 (m, 4H). – ^{13}C NMR (CD_3CN, 263 K): CH_2 δ = 24.1, 24.3, 25.7, 26.0, 26.4, 26.6, NCH_2 46.1, 46.7, 47.0 (2C), C=O, C=N 182.4, 163.5, 158.1, 155.7, 14 signals for aromatic C.

$[C_{30}H_{32}N_5O]SbCl_6$ (813.1) Calcd. C 44.31 H 3.97 N 8.62 Found C 44.49 H 4.10 N 8.72

2,4-Bis(diisopropylamino)-6-[(1-naphthylphenylmethylene)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**7m**): From diisopropylcyanamide (1.27 g, 10.06 mmol) as described for **7k**. Recrystallization from dichloromethane (5 ml)/pentane (12 ml) afforded yellow crystals (3.32 g, 79%); m.p. 147–152 °C. – IR: 1680, 1600, 1560 cm^{-1}. – ^1H NMR (CD_2Cl_2, 300 K): CH_3 δ = 0.84 (d, J = 7 Hz), 1.24 (d, J = 7 Hz), 1.31 (d, J = 7 Hz), 1.39 (d, J = 7 Hz), CH 3.85, 3.98, 4.22, 4.53 (m's, broad). – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 19.8, 20.1, 20.3, 21.1, CH 48.8, 49.7 (2C), 50.5, C=O, C=N 181.7, 161.6, 158.1, 155.7, 14 signals for aromatic C.

$[C_{32}H_{40}N_5O]SbCl_6$ (845.2) Calcd. C 45.47 H 4.77 N 8.29 Found C 45.61 H 4.82 N 8.23

2,4-Bis(diisopropylamino)-6-(2,2-dimethyl-1-phenylpropylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (**7n**): From **1n**[30] (1.12 g, 5.00 mmol), antimony pentachloride (1.50 g, 5.00 mmol), and diisopropylcyanamide (1.27 g, 10.06 mmol) as described for **7b**. Yield 2.79 g (72%) of a colourless powder; m.p. 205–210°C (dec.). – IR:1690, 1640, 1600, 1550 cm^{-1}. – ^1H NMR ($CDCl_3$, 303 K): CH_3 δ = 1.24 (d, *J* = 7 Hz), 1.32 (d, *J* = 7 Hz), 1.35, 1.43 (d, *J* = 7 Hz). – ^{13}C NMR ($CDCl_3$, 303 K): CH_3 δ = 19.7, 20.0, 20.8, 21.2, 28.1, C 42.2, CH 48.4, 49.5, 49.6, 50.3, C=N, C=O 195.4, 161.2, 157.6, 155.1, phenyl 134.9, 130.4, 128.7, 125.6.

$[C_{26}H_{42}N_5O]SbCl_6$ (775.1) Calcd. C 40.29 H 5.46 N 9.04 Found C 40.22 H 5.50 N 9.03

2-[(1-tert-Butyl-2,2-dimethylpropylidene)amino]-4,6-bis(diisopropylamino)-1,3,5-oxadiazinium Hexachloroantimonate (**7o**): From **1o**[1] (1.02 g, 5.00 mmol), antimony pentachloride (1.50 g, 5.00 mmol), and diisopropylcyanamide (1.27 g, 10.06 mmol) as described for **7b**. Addition of anhydrous ether (25 ml) to the reaction mixture afforded yellow crystals (2.87 g, 76%); m.p. 214–218°C (dec.). – IR: 1750, 1640, 1570 cm^{-1}. – ^1H NMR (CD_2Cl_2, 303 K): $(CH_3)_3$ δ = 1.42, CH 3.97 (sept, *J* = 7 Hz), 4.50 (2H, m, broad), 4.70 (sept, *J* = 7 Hz). – ^{13}C NMR (CD_2Cl_2, 303 K): CH_3 δ = 19.8, 20.4, 21.0, 21.4, 30.0, C 45.9, CH 48.3, 49.3, 49.5, 50.4, C=N, C=O 195.8, 158.8, 157.2, 155.5.

$[C_{24}H_{46}N_5O]SbCl_6$ (755.1) Calcd. C 38.17 H 6.14 N 9.28 Found C 38.40 H 6.31 N 9.30

1-tert-Butyl-3-(dimethylamino)-3-{[(dimethylamino)isocyanatomethylene]amino}-1-phenyl-2-azaallenium Hexachloroantimonate (**11**): From dimethylcyanamide (0.71 g, 10.13 mmol) as described for **7a**. The product was precipitated at –25°C with anhydrous ether (50 ml)/pentane (20 ml) affording yellow needles (2.82 g, 85%); m.p. 158–161°C (dec.). – IR: NCO 2240, 1620, 1570 cm^{-1}. – ^1H NMR (CD_3CN, 263 K): $(CH_3)_3$ δ = 1.30, CH_3 2.69, 2.97, 3.13, 3.24. – ^{13}C NMR (CD_3CN, 263 K): $(CH_3)_3$ 27.9, NCH_3, C 38.9, 39.2, 39.3, 40.4, 42.3, NCO 127.5, C=N 190.9, 162.9, 147.6, *ipso,p*-C 136.0, 130.4, *o,m*-C 129.3, 125.6.

$[C_{18}H_{26}N_5O]SbCl_6$ (662.9) Calcd. C 32.61 H 3.95 N 10.57 Found C 32.43 H 3.95 N 10.58

1-tert-Butyl-3-(dimethylamino)-3-{[(dimethylamino)[(methoxycarbonyl)amino]methylene]amino}-1-phenyl-2-azaallenium Hexachloroantimonate (**12**): To **11** (1.99 g, 3.00 mmol) in anhydrous dichloromethane (20 ml) dry methanol (0.39 g, 12.0 mmol) was added. After stirring for 10 h at 22°C the reaction mixture was cooled to –25°C. Slow addition of ether (60 ml) afforded a pale yellow precipitate (1.52 g, 73%); m.p. 160–163°C. – IR: 3350, 1760, 1620, 1570 cm^{-1}. – ^1H NMR (CD_3CN, 263 K): CH_3 δ = 1.21, 2.48, 3.02, 3.09, 3.11, 3.76, NH 8.42. – ^{13}C NMR (CD_3CN, 263 K): CH_3 δ = 27.8, 38.7, 39.0, 39.7, 42.2, 54.1, C=O, C=N 188.3, 164.5, 152.6, 152.4, *ipso,p*-C 136.2, 130.3, *o,m*-C 129.4, 125.9.

$[C_{19}H_{30}N_5O_2]SbCl_6$ (695.0) Calcd. C 32.84 H 4.35 N 10.08 Found C 32.79 H 4.38 N 10.05

2-tert-Butyl-4,6-bis(dimethylamino)-2,3-dihydro-2-phenyl-1,3,5-triazinium Hexachloroantimonate (**13**): A mixture of **11** (1.99 g, 3.00 mmol) with water (0.22 g, 12.0 mmol) in dichloromethane (20 ml) was stirred for 10 h at 22°C. After drying over sodium sulfate ether (60 ml) was added affording yellow crystals (1.80 g, 94%); m.p. 220–225°C (dec.). – IR: 1630, 1580 cm^{-1}. – ^1H NMR (CD_3CN/CD_2Cl_2 2:1, 263 K): CH_3 δ = 1.07, 3.07, 3.23, NH 6.51 (2H). – ^{13}C NMR (CD_3CN/CD_2Cl_2 2:1, 263 K): CH_3 δ = 25.0, 37.8, 38.2, C 38.2 (?), 77.8, C=N 156.6, phenyl 140.0, 129.2, 128.4, 128.1.

$[C_{17}H_{28}N_5]SbCl_6$ (639.9) Calcd. C 32.06 H 4.43 N 11.00 Found C 32.24 H 4.28 N 11.07

2,4-Bis(dimethylamino)-6-[(methoxydiphenylmethyl)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**8a**): A solution of **7a** (3.42 g, 5.00 mmol) in anhydrous methanol (10 ml) and anhydrous dichloromethane (10 ml) was stirred for 3 h at 22°C. With ether (50 ml) a yellow powder was precipitated (3.22 g, 90%); m.p. 129–132°C. – IR: 1710, 1620 cm^{-1}. – ^1H NMR (CD_3CN,

263 K): CH_3 δ = 2.44, 3.02, 3.16, 3.22, 3.31, NH 8.38. – ^{13}C NMR (CD_3CN, 263 K): CH_3 δ = 36.7, 37.0, 37.3, 37.5, OCH_3 51.3, C 91.7, C=O, C=N 159.4, 156.5, 155.6, phenyl 142.9, 129.4, 128.5, 126.1.

$[C_{21}H_{26}N_5O_2]SbCl_6$ (714.9) Calcd. C 35.28 H 3.67 N 9.80 Found C 35.33 H 3.69 N 9.67

2,4-Bis(diisopropylamino)-6-[(methoxydiphenylmethyl)amino]-1,3,5-oxadiazinium Hexachloroantimonate (**8d**): From **7d** (3.98 g, 5.00 mmol) as described for **8a**. After addition of anhydrous ether (80 ml) to the reaction mixture pale yellow needles (3.22 g, 78%) crystallized at –78°C; m.p. 143–145°C. – IR: 1690, 1570 cm^{-1}.

$[C_{29}H_{42}N_5O_2]SbCl_6$ (827.1) Calcd. C 42.11 H 5.12 N 8.47 Found C 42.02 H 5.08 N 8.33

2-{[(4-Bromophenyl)methoxyphenylmethyl]amino}-4,6-bis(dimethylamino)-1,3,5-oxadiazinium Hexachloroantimonate (**8p**): To **1p**[30] (1.61 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) was added at –78°C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) and a solution of dimethylcyanamide (0.71 g, 10.13 mmol) in anhydrous dichloromethane (10 ml). The mixture was stirred for 4 h at 22°C. After evaporation of the solvent the oily product was dissolved in anhydrous dichloromethane (10 ml) and methanol (8 ml). The solution was stirred for 5 h. After addition of anhydrous ether (60 ml)/pentane (50 ml) at –25°C yellow prisms crystallized (1.39 g, 35%); m.p. 125–129°C. – IR: 1710, 1620, 1610 cm^{-1}. – ^1H NMR (CD_2Cl_2): NCH_3 δ = 3.18 (broad), OCH_3 3.39, NH 7.15. – ^{13}C NMR (CD_2Cl_2): OCH_3 δ = 51.8, OCN 91.8, C=O, C=N 162.1, 159.6, 156.6.

$[C_{21}H_{25}BrN_5O_2]SbCl_6$ (793.8) Calcd. C 31.77 H 3.18 N 8.82 Found C 31.92 H 3.19 N 8.85

1-(Diphenylmethyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17a**): To **1a** (1.22 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) was added at –78°C with stirring a solution of antimony pentachloride (1.50 g, 5.00 mmol) in anhydrous dichloromethane (10 ml), followed by a solution of diisopropylcarbodiimide (1.27 g, 10.06 mmol) in anhydrous dichloromethane (10 ml). Stirring was continued for 2 h at 22°C. Dropwise addition of anhydrous ether (50 ml) afforded a precipitate, which was recrystallized from dichloromethane (5 ml)/ether giving colourless needles (4.05 g, 92%); m.p. 111–113°C. – IR: 1750, 1690, 1540 cm^{-1}. – ^1H NMR (CD_2Cl_2, 263 K): CH_3 δ = 1.33 (d, *J* = 7 Hz), 1.52 (d, *J* = 7 Hz), 1.56 (d, *J* = 7 Hz), 1.85, CH 3.85 (sept, *J* = 7 Hz, 2H), 4.26 (sept, *J* = 7 Hz, 1H), CHN 6.28. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 20.0, 20.7, 23.8, 28.2, CH 50.6, 56.5, 57.6, 67.3, phenyl 128.4, 129.2, 129.4, 146.1, C=O, C=N 188.0, 159.3, 146.1, 130.9.

$[C_{28}H_{38}N_5O]SbCl_6 \cdot CH_2Cl_2$ (880.0) Calcd. C 39.58 H 4.58 N 7.96
Found C 39.52 H 4.61 N 7.98

1-(Diphenylmethyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Tetrachloroferrate (**17b**): To anhydrous $FeCl_3$ (0.81 g, 5.00 mmol) in anhydrous dichloromethane (10 ml) was added at –20°C with stirring a solution of **1a** (1.22 g, 5.00 mmol) in dry dichloromethane (10 ml) and a solution of diisopropylcarbodiimide (1.27 g, 10.06 mmol) in anhydrous dichloromethane (10 ml). The reaction mixture was stirred for 5 h at 22°C and filtered with exclusion of moisture. Slow addition of anhydrous ether (50 ml) afforded greenish crystals (3.04 g, 93%); m.p. 124–126°C. – IR: 1750, 1690, 1540 cm^{-1}.

$[C_{28}H_{38}N_5O]FeCl_4$ (658.3) Calcd. C 51.08 H 5.82 N 10.64 Found C 51.12 H 5.89 N 10.57

1-(Diphenylmethyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Trichlorozincate (**17c**): As described for **17b** with anhydrous zinc chloride (0.68 g, 5.00 mmol) instead of $FeCl_3$. Yield 3.07 g (97%) of a colourless powder; m.p. 156–161°C. – IR: 1750, 1690, 1540 cm^{-1}.

$[C_{28}H_{38}N_5O]ZnCl_3$ (632.4) Calcd. C 53.18 H 6.06 N 11.08 Found C 52.86 H 6.05 N 10.96

3,5-Dicyclohexyl-6-(cyclohexylideneamino)-4-(cyclohexylimino)-1-(diphenylmethyl)-2,3,4,5-tetrahydro-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17d**): From dicyclohexylcarbodiimide (2.07 g, 10.05 mmol) in analogy to **17a**. After 3 h stirring at 22°C the product was precipitated with anhydrous pentane (50 ml) affording a pale yellow powder (4.89 g, 98%); m.p. 118–119°C (dec.). – IR: 1750, 1690, 1530 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): CH δ = 58.3, 64.7, 66.0, 67.7, C=O, C=N 192.5, 159.2, 146.3, 131.3.

$[C_{40}H_{54}N_5O]SbCl_6 \cdot 1/2\ CH_2Cl_2$ (997.8) Calcd. C 48.75 H 5.56 N 7.02
Found C 48.72 H 5.69 N 7.06

3,5-Dicyclohexyl-6-(cyclohexylideneamino)-4-(cyclohexylimino)-1-(diphenylmethyl)-2,3,4,5-tetrahydro-2-oxo-1,3,5-triazinium Tetrachloroferrate (**17e**): As described for **17b** from dicyclohexylcarbodiimide (2.07 g, 10.05 mmol). Yield 3.32 g (81%) of a yellow powder; m.p. 165–166°C. – IR: 1750, 1680, 1530 cm^{-1}.

$[C_{40}H_{54}N_5O]FeCl_4$ (818.6) Calcd. C 58.69 H 6.65 N 8.56 Found C 58.09 H 6.64 N 8.40

1-(9-Fluorenyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17f**): From **1g** (1.21 g, 5.00 mmol) in analogy to **17a**. Yield after recrystallization 2.34 g (59%) of yellow needles; m.p. 138–139°C. – IR: 1760, 1680, 1530 cm^{-1}.

$[C_{28}H_{36}N_5O]SbCl_6$ (793.1) Calcd. C 42.40 H 4.58 N 8.83 Found C 42.52 H 4.52 N 8.75

1-(9-Fluorenyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Tetrachloroferrate (**17g**): From **1g** (1.21 g, 5.00 mmol) as described for **17b**. Precipitation with pentane (50 ml) yielded an oil, which was dissolved in dichloromethane (5 ml)/pentane (3 ml). At –80°C a pale yellow powder crystallized (2.20 g, 67%); m.p. 140–142°C. – IR: 1750, 1690, 1530 cm^{-1}.

$[C_{28}H_{36}N_5O]FeCl_4$ (656.3) Calcd. C 51.24 H 5.53 N 10.67 Found C 51.24 H 5.52 N 10.71

1-(9-Fluorenyl)-2,3,4,5-tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-2-oxo-1,3,5-triazinium Trichlorozincate (**17h**): In analogy to **17f** with anhydrous zinc chloride (0.68 g, 5.00 mmol) instead of antimony pentachloride. Yield (without recrystallization) 2.68 g (75%) of a colourless powder; m.p. 136–138°C. – IR: 1740, 1690, 1530 cm^{-1}. – ^1H NMR (CD_3COCD_3): CH_3 δ = 1.36 (d, *J* = 7 Hz), 1.41 (d, *J* = 7 Hz), 1.48, 1.75 (d, *J* = 7 Hz), CH 4.10 (sept, *J* = 7 Hz, 1H), 4.22 (sept, *J* = 7 Hz, 2H), 6.71, aromatic H 7.47 (t, *J* = 7 Hz), 7.57 (t, *J* = 7 Hz), 7.69 (d, *J* = 8 Hz), 7.98 (d, *J* = 7 Hz). – ^{13}C NMR (CD_3COCD_3): CH_3 δ = 20.2, 20.9, 24.1, 28.0, CH 50.7, 56.5, 57.3, 60.5, C=O, C=N 186.3, 156.9, 149.0, 131.7, aromatic C 141.1, 140.6, 130.4, 129.2, 125.9, 121.6.

$[C_{28}H_{36}N_5O]ZnCl_3 \cdot CH_2Cl_2$ (715.3) Calcd. C 48.69 H 5.36 N 9.79
Found C 49.06 H 5.47 N 9.88

3,5-Dicyclohexyl-6-(cyclohexylideneamino)-4-(cyclohexylimino)-1-(9-fluorenyl)-2,3,4,5-tetrahydro-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17i**): As described for **17b** from dicyclohexylcarbodiimide (2.07 g, 10.05 mmol). Yield 3.12 g (66%) of orange crystals; m.p. 130°C. – IR: 1740, 1690, 1520 cm^{-1}. – ^1H NMR (CD_2Cl_2, 303 K): CH δ = 3.22 (m), 3.50 (m), 3.74 (m), 6.59. – ^{13}C NMR (CD_2Cl_2): CH_2 δ = 24.0, 24.4, 25.2, 25.4, 25.8, 26.6, 27.0, 27.3, 30.0, 31.2, 34.1, 38.2, CH 58.6, 60.4, 64.3, 66.3, C=O, C=N 189.8, 155.6, 148.5, 130.9, aromatic C 140.5, 139.5, 130.4, 129.2, 124.9, 121.3.

$[C_{40}H_{52}N_5O]SbCl_6$ (953.3) Calcd. C 50.39 H 5.50 N 7.35 Found C 50.46 H 5.78 N 7.34

2,3,4,5-Tetrahydro-3,5-diisopropyl-6-(isopropylideneamino)-4-(isopropylimino)-1-(1-naphthylphenylmethyl)-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17j**): From **1k** (1.47 g, 5.00 mmol) as described for **17d**. Yield after recrystallization from dichloromethane (5 ml)/pentane

(3 ml) 2.47 g (59%) of an ochreous powder; m.p. 89–90°C. – IR: 1750, 1690, 1540 cm^{-1}. – ^1H NMR (CD_2Cl_2, 263 K): CH_3 δ = 1.17 (d, *J* = 6 Hz), 1.29 (d, *J* = 6 Hz), 1.38 (d, *J* = 7 Hz), 1.46, 1.49 (d, *J* = 7 Hz), 1.57 (d, *J* = 7 Hz), 1.61 (d, *J* = 7 Hz), 1.88, CH 3.78 (m, 2H), 3.92 (sept, *J* = 7 Hz, 1H), 6.93. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 19.8, 20.1, 20.6, 20.7, 23.6, 23.7, 27.9, 28.5, CH 50.5, 56.6, 57.5, 65.1, C=O, C=N 187.9, 158.9, 146.0, 133.8 (?), 14 aromatic C.

$[C_{32}H_{40}N_5O]SbCl_6$ (845.2) Calcd. C 45.47 H 4.77 N 8.29 Found C 45.55 H 4.90 N 8.31

3,5-Dicyclohexyl-6-(cyclohexylideneamino)-4-(cyclohexylimino)-2,3,4,5-tetrahydro-1-(1-naphthylphenylmethyl)-2-oxo-1,3,5-triazinium Hexachloroantimonate (**17k**): From dicyclohexylcarbodiimide (2.07 g, 10.05 mmol) as described for **17j**. Recrystallization from dichloromethane (10 ml)/ether (30 ml) afforded a pale yellow powder (4.02 g, 80%); m.p. 134°C (dec.). – IR: 1750, 1690, 1530 cm^{-1}.

$[C_{44}H_{56}N_5O]SbCl_6$ (1005.4) Calcd. C 52.56 H 5.61 N 6.97 Found C 52.72 H 5.68 N 6.95

2,3,4,5-Tetrahydro-1,3,5-triisopropyl-6-[isopropyl(2,2-dimethyl-1-phenylpropylidenecarbamoyl)amino]-2,4-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**20n**): From **1n** (1.12 g, 5.00 mmol), antimony pentachloride (1.50 g, 5.00 mmol), and diisopropylcarbodiimide (1.90 g, 15.06 mmol) as described for **17a**. The oily product was dissolved in dichloromethane (10 ml)/methanol (10 ml). Addition of ether (50 ml)/pentane (30 ml) and cooling to –25°C afforded colourless crystals (2.75 g, 61%); m.p. 148–149°C (dec.). – IR: 1670, 1530 cm^{-1}. – ^1H NMR ($CDCl_3$): CH_3 δ = 1.11 (d, *J* = 6 Hz), 1.19 (d, *J* = 6 Hz), 1.20 (d, *J* = 6 Hz), 1.23 (d, *J* = 6 Hz), 1.30, 1.50 (d, *J* = 6 Hz), 1.57 (d, *J* = 7 Hz), CH 3.29 (sept, *J* = 6 Hz, 1H), 4.23 (m, 5H). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 20.7, 21.2, 21.7, 21.8, 23.0, 23.3, 28.0 (3C), CH, C 42.1, 50.9, 54.8, 54.9, 58.1, C=O, C=N 190.0, 160.6, 156.5, 135.4, phenyl 135.5, 129.3, 128.2, 126.3.

$[C_{33}H_{56}N_7O]SbCl_6$ (901.3) Calcd. C 43.97 H 6.26 N 10.88 Found C 44.05 H 6.09 N 10.81

6-[(1-tert-Butyl-2,2-dimethylpropylidenecarbamoyl)isopropylamino]-2,3,4,5-tetrahydro-1,3,5-triisopropyl-2,4-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**20o**): From **1o** (1.02 g, 5.00 mmol) as described for **20n**. The oily product crystallized from a mixture of dichloromethane (10 ml)/methanol (10 ml)/ether (80 ml) at –25°C. Yield 2.56 g (58%) of colourless needles; m.p. 137–138°C. – IR: 1660, 1630, 1610 cm^{-1}. – ^1H NMR (CD_3CN, 333 K): CH_3 δ = 1.18 (d, *J* = 6 Hz), 1.23 (d, *J* = 6 Hz), 1.25 (d, *J* = 6 Hz), 1.38 (d, *J* = 7 Hz), 1.40 (18H), 1.57 (d, *J* = 7 Hz), 1.62 (d, *J* = 7 Hz), CH 3.45 (broad, 1H), 4.13 (broad, 1H), 4.32 (sept, *J* = 6 Hz, 2H), 4.68 (sept, *J* = 7 Hz, 2H). – ^{13}C NMR (CD_3CN, 333 K): CH_3 δ = 21.3, 21.6, 22.0, 22.1, 23.4, 23.7, 30.3 (*t*Bu), CH, C 45.4, 51.5, 54.5, 56.2, 58.3, C=O, C=N 194.8, 158.0, 157.7, 137.1.

$[C_{31}H_{60}N_7O]SbCl_6$ (881.3) Calcd. C 42.24 H 6.86 N 11.13 Found C 42.12 H 6.89 N 11.10

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