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Synthesis and Structure of Heterocumulenes with $>C=\overset{+}{N}=C=O$ and $>C=\overset{+}{N}=C=S$ Units

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Preparations, IR and NMR spectra of 1-oxa-3-azabutatrienium hexachloroantimonates (**2a – f**) and of 1-thia-3-azabutatrienium hexachloroantimonate **2g** are reported. According to an *X*-ray structure analysis of **2b, g** these compounds crystallize as pseudocumulenes with bent $C=N=C=X$ units (∢ $C=N=C$ 129° for X = O and 139° for X = S). The extremely moisture sensitive salts **2a – e** react with water to give the iminium salts **3**, while **2g** gives benzophenone. With carboxylic acids the 1-oxabutatrienium salts **2a – e** afford carboxylic anhydrides (e.g. **4**) and the iminium salts **3a – e**. The α-naphthyl compound **2c** cyclizes to give the isoquinolinium salt **5**. With *N,N*-dimethylaniline **2a, e, g** afford triarylcarbenium dyes (**8**).

Synthese und Molekülstrukturen von Heterokumulenen mit $>C=\overset{+}{N}=C=O$- und $>C=\overset{+}{N}=C=S$-Einheiten

Es wird über Synthesen, IR- und NMR-Spektren der 1-Oxa-3-azabutatrienium-hexachloroantimonate **2a – f** und des 1-Thia-3-azabutatrienium-hexachloroantimonats **2g** berichtet. Nach Röntgenstrukturanalysen von **2b, g** kristallisieren diese Verbindungen als Pseudokumulene mit gewinkelten $C=N=C=X$-Einheiten (∢ $C=N=C$ 129° für X = O und 139° für X = S). Die extrem feuchtigkeitsempfindlichen Salze **2a – e** reagieren mit Wasser zu den Iminiumsalzen **3**, Verbindung **2g** dagegen zu Benzophenon. Die 1-Oxabutatrienium-Salze **2a – e** reagieren mit Carbonsäuren zu deren Anhydriden und den Iminiumsalzen **3a – e**. Das α-Naphthylderivat **2c** cyclisiert zum Isochinolinium-Salz **5**. Mit *N,N*-Dimethylanilin erhält man aus **2a, e, g** die Triarylcarbenium-Farbstoffe **8**.

Recent interest in the chemistry of α-chloro isocyanates and isothiocyanates and the observation that these compounds exhibit ionic properties[1,2] prompted us to prepare representatives of the hitherto unknown class of heterobutatrienium salts **2**.

On addition of antimony pentachloride to a solution of chlorodiphenylmethyl isocyanate (**1a**)[1,2] in dichloromethane or acetonitrile at temperatures below −10°C a yellow precipitate **2a** is formed, which proved to be extremely moisture sensitive and reactive against nucleophiles. **2a** is stable at room temperature if water is thoroughly excluded. Above 100°C the yellow colour of **2a** gradually turns dark. The compound decomposes without melting.

The ^{13}C NMR spectrum of **2a** shows only four signals for the aromatic carbons, which can be assigned from a gated decoupling experiment (*i*-C δ = 136.1, *o*-C 139.3, *m*-C 131.6, *p*-C 144.6 (CD_3CN, 263 K)), and two additional signals at δ = 200.5 and 133.8. In the gated decoupling

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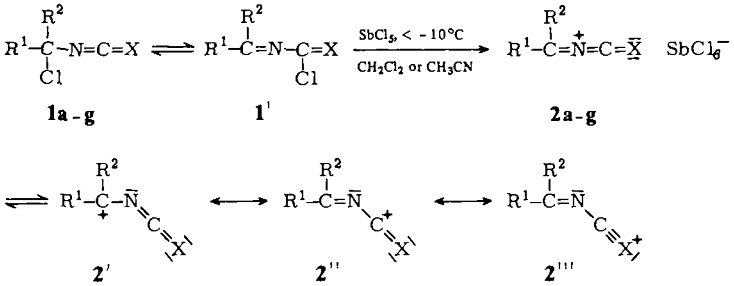
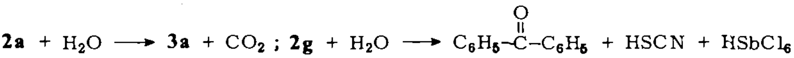


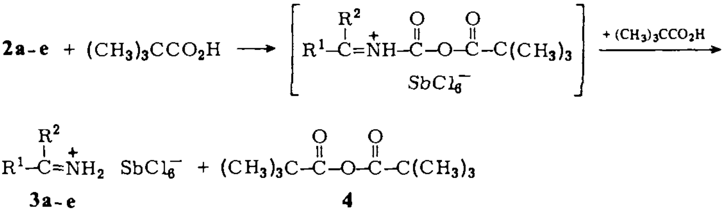
$R^1-\underset{Cl}{\overset{R^2}{C}}-N=C=X \rightleftharpoons R^1-\overset{R^2}{C}=N-\underset{Cl}{C}=X \xrightarrow[CH_2Cl_2 \text{ or } CH_3CN]{SbCl_5,\ < -10^\circ C} R^1-\overset{R^2}{C}=\overset{+}{N}=C=X\quad SbCl_6^-$

1a-g **1'** **2a-g**

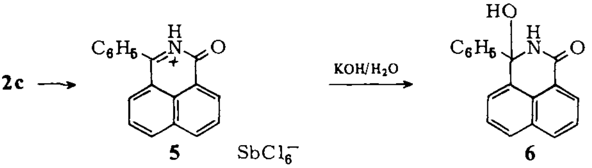
2' **2''** **2'''**



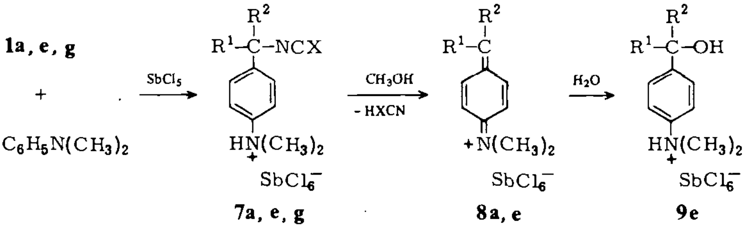
$$\mathbf{2a} + H_2O \longrightarrow \mathbf{3a} + CO_2\ ;\ \mathbf{2g} + H_2O \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5 + HSCN + HSbCl_6$$



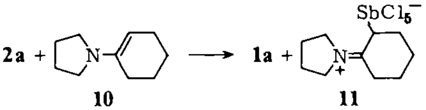
3a-e **4**



5 **6**



7a, e, g **8a, e** **9e**



10 **11**

	R^1	R^2	X
a	C_6H_5	C_6H_5	O
b	4-BrC_6H_4	C_6H_5	O
c	1-$C_{10}H_7$	C_6H_5	O
d	$(CH_3)_3C$	C_6H_5	O

	R^1	R^2	X
e	2-C_6H_4–C_6H_4-2'		O
f	$(CH_3)_3C$	$(CH_3)_3C$	O
g	C_6H_5	C_6H_5	S

spectrum the line at $\delta = 133.8$ appears as a sharp singlet while the resonance at $\delta = 200.5$ forms a broad triplet ($J \approx 3$ Hz). According to these spectra the yellow compound **2a** should be 4,4-diphenyl-1-oxa-3-azabutatrienium hexachloroantimonate with either a linear $C=N=C=O$ moiety (**2a**) or a bent isocyanato-α-carbenium geometry (**2′a** ↔ **2″a** ↔ **2‴a**) showing at −10 °C fast rotation around the $C-N$ single bond or, more likely, fast inversion at the nitrogen atom, in order to explain the magnetic equivalence of the two phenyl substituents at this temperature.

In CH_2Cl_2 the antisymmetric NCO stretching vibration of **1a** is found at 2239 cm^{-1}. Strong bands for $C=N$ and $C=O$ of form **1′a** are observed at 1620 and 1740 cm^{-1}. On addition of $SbCl_5$ (in CH_2Cl_2) these absorptions disappear completely and new strong and sharp bands are observed at 2218, 1660, and 1580 cm^{-1} together with weaker bands at 1800 and 2330 cm^{-1}. The latter band is propably to be assigned to CO_2, which stems from the hydrolysis of part of **2a**. The band at 2218 cm^{-1} must be assigned to the antisymmetric $C=N=C=O$ stretching vibrations thus supporting the structural proposal for **2a**. In contact with air or on addition of a trace of water to its solution **2a** is immediately hydrolyzed to the iminium salt **3a**.

The salt **2a** readily reacts with carboxylic acids. With two equivalents of pivalic acid the iminium salt **3a** (98%) and pivalic anhydride (**4**) are formed. These reactions suggest the structure of a stabilized acylium salt **2″a** ↔ **2‴a** for the yellow precipitate rather than that of an α-carbenium isocyanate **2′a**, which should react with OH containing molecules to give benzophenone instead of **3a**.

For the yellow salt **2b**, which was formed from the α-chloro isocyanate **1b**[1] with antimony pentachloride, an *X*-ray diffraction analysis was carried out (see below), which confirmed the proposed structure **2b**.

When a solution of the violet salt **2c** [IR(CH_2Cl_2): CNCO 2205 cm^{-1}] in dichloromethane was left for some time at +5 °C an intramolecular electrophilic aromatic substitution took place affording orange prisms of the heterocycle **5**, which reacted with aqueous potassium hydroxide to give the known hemiacetal **6**[3]. The *peri*-substitution in **5** also follows from the 250 MHz ^1H NMR spectrum, which shows two triplets, each coupled to two doublets, in the region for the aromatic protons.

With pivalic acid **2c** forms the iminium salt **3c** in a fast reaction.

The aliphatic substituted butatrienium salts **2d, f** are thermally labile. At +23 °C the yellow solution of **2d** [IR(CH_2Cl_2): CNCO 2235 cm^{-1}] in dichloromethane soon became colourless, and then slowly turned dark. With pivalic acid the iminium salt **3d** was obtained.

In the ^{13}C NMR spectrum of the yellow reaction mixture of **1f**[2] and antimony pentachloride in CD_3CN (233 K) more than seventy lines were recorded indicating fast decomposition of the unstable cumulene. Addition of pivalic acid to a suspension of **2f** in dichloromethane afforded a mixture of compounds containing **3f**.

On treatment of the α-chloro isothiocyanate **1g**[4] with antimony pentachloride in anhydrous dichloromethane or acetonitrile at −20 °C an orange salt is formed, for which structure **2g** was proven by an *X*-ray diffraction analysis (see below).

A cation of type **2g** has recently been obtained by *Maas* et al.[5] by an independent method.

The moisture sensitive and thermally unstable cumulene **2g** shows overlapping strong IR absorptions (CH_2Cl_2) at 1980, 1930, and 1890 cm^{-1}. An equilibrium **1g** + $SbCl_5 \rightleftharpoons$ **2g** can be excluded from the fact that in the ^{13}C NMR spectrum (CH_3CN, 263 K) of **2g** only four lines for the phenyl groups are observed indicating the presence of only one compound in solution. According to the equivalence of the phenyl substituents the CNCS unit of **2g** must either be linear or bent showing fast topomerization at the nitrogen atom. The signal for C=N was found at δ = 194.8. A broad resonance at 135.0 must be attributed to NCS.

The salt **2g** is less reactive than the oxa analogue **2a**. While **2a** reacts with water to give the iminium salt **3a** the isothiocyanate **2g** affords exclusively benzophenone. Contrary to **2a**, compound **2g** does not react with carboxylic acids at room temperature. These differences may indicate that for **2a** the canonical forms **2''** ↔ **2'''** are most important while **2g** is best described by the isothiocyanato carbenium formula **2'**.

The heterobutatrienium salts **2a, e, g** react with *N,N*-dimethylaniline to give the triarylcarbenium dyestuffs **8a, e**. The UV spectrum of **8a** is very similar to that of the corresponding chloride[6)]. Thus, water and *N,N*-dimethylaniline react at different sites of the ambident electrophiles **2**.

One may speculate that in the case of the aniline the first step of the reaction is actually an *N*-acylation followed by a rearrangement to the *C*-alkylation product **7**.

The rather unstable salts **7a, e** were isolated [**7a**: NCO 2260 $\mathrm{cm^{-1}}$, **7e**: 2240 $\mathrm{cm^{-1}}$ (CH_2Cl_2)]. In the ^1H NMR spectrum of **7a** a spin-spin coupling between NH and CH_3 was observed. In methanol compounds **7** are decomposed to **8**.

Compound **8e** is sparingly soluble in all usual organic solvents. But a suspension of **8e** in dimethyl sulfoxide gives a brown solution of the carbinol **9e** on addition of a drop of water.

The formation of **2** can be reversed in the presence of an amine: In the reaction of **2a** with the enamine **10** only **1a** and a complex possibly of the constitution **11** of an antimony pentachloride adduct with **10** were obtained.

X-Ray Diffraction Analyses of 2b and 2g*)

2b, $[C_{14}H_9BrNO]^+[SbCl_6]^-$, triclinic, space group $P\bar{1}$ (No. 2[7)]), Z = 2, a = 958.0(4), b = 1039.1(5), c = 1060.6(4) pm, α = 91.62(3)°, β = 97.48(3)°, γ = 72.65(3)°, $V = 999 \cdot 10^6$ $\mathrm{pm^3}$, $d_{\mathrm{calc.}}$ = 2.07 $\mathrm{gcm^{-3}}$, $\mu_{\mathrm{Mo}\text{-}K_\alpha}$ = 43.1 $\mathrm{cm^{-1}}$, T = 243 K, ω-scan, $\Delta\omega$ = 1.1°, $2.0 < \dot{\omega} <$ 29.3° $\mathrm{min^{-1}}$, $2° < 2\Theta < 42°$, 1905 independent significant reflections ($I \geqslant 2\sigma(I)$). The cell constants and the reflections were measured on a Syntex-P3 diffractometer with a graphite monochromator, $\lambda_{\mathrm{Mo}\text{-}K_\alpha}$ = 71.069 pm. The structure was solved using the programme SHEL-XTL[8)] by direct methods. Hydrogen atoms were fixed on calculated geometrically ideal positions. The partially anisotropic refinement led to agreement factors R_1 = 0.037 and R_2 = 0.042.

A list of atomic coordinates with LS-computed standard deviations is given in Table 1. Fig. 1 shows a plot with selected bond lengths of the cation of **2b**.

2g, $[C_{14}H_{10}NS]^+[SbCl_6]^-$, monoclinic, space group $P2_1/c$ (No. 14[7)]), Z = 4, a = 811.6(4), b = 1268.6(5), c = 2142.8(8) pm, β = 116.26(4)°, $V = 1979 \cdot 10^6$ $\mathrm{pm^3}$, $d_{\mathrm{calc.}}$ = 1.88 $\mathrm{gcm^{-3}}$, $\mu_{\mathrm{Mo}\text{-}K_\alpha}$ = 23.1 $\mathrm{cm^{-1}}$, T = 233 K, ω-scan, $\Delta\omega$ = 1.0°, $2.9 < \dot{\omega} < 29.3$, $2° \leqslant 2\Theta \leqslant 42°$, 1507 independent significant reflections ($I \geqslant 2\sigma$). Measurements and solution as described for **2b**. The anisotropic refinement with full matrix led to agreement factors R_1 = 0.056 and R_2 = 0.063.

A list of atomic coordinates with LS-computed standard deviations is given in Table 2. Fig. 2 shows a molecular plot and bond lengths for the cation **2g**. In Table 3 selected bond angles and torsional angles for the cations **2b, g** are presented.

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*) 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 registry number CSD 50645, authors, and source.

Table 1. Fractional Atomic Coordinates and Temperature Parameters for **2b**[a]

atom	x/a	y/b	z/c	K	U
Sb1	0.50000(0)	1.00000(0)	1.50000(0)	0.5	
Cl1	0.7635(2)	0.9274(2)	1.5211(2)	1.0	
Cl2	0.5071(3)	0.8499(2)	1.6681(2)	1.0	
Cl3	0.4939(2)	0.8272(2)	1.3507(2)	1.0	
Sb2	0.50000(0)	0.50000(0)	1.00000(0)	0.5	
Cl1X	0.5779(3)	0.2639(2)	1.0325(3)	1.0	
Cl2X	0.2819(5)	0.4772(5)	0.8846(6)	0.6	
Cl2Y	0.681(1)	0.472(1)	0.862(2)	0.4	
Cl3X	0.6062(9)	0.4766(9)	0.8102(7)	0.6	
Cl3Y	0.672(1)	0.5196(7)	1.1744(8)	0.4	
Br	0.8787(1)	-0.2895(1)	0.9103(1)	1.0	
N	1.1729(8)	0.2060(8)	0.7665(7)	1.0	
O	1.3806(7)	0.0775(7)	0.9043(6)	1.0	
C1	1.277(1)	0.1338(9)	0.8393(9)	1.0	0.034(2)
C2	1.0378(9)	0.1937(9)	0.7323(8)	1.0	0.027(2)
C3	0.937(1)	0.3029(9)	0.6595(8)	1.0	0.029(2)
C4	0.955(1)	0.432(1)	0.6621(9)	1.0	0.039(3)
C5	0.854(1)	0.536(1)	0.590(1)	1.0	0.052(3)
C6	0.740(1)	0.511(1)	0.511(1)	1.0	0.056(3)
C7	0.720(1)	0.384(1)	0.503(1)	1.0	0.051(3)
C8	0.816(1)	0.2803(9)	0.5779(9)	1.0	0.035(2)
C9	0.9984(9)	0.0776(9)	0.7705(8)	1.0	0.027(2)
C10	0.864(1)	0.0954(9)	0.8143(8)	1.0	0.031(2)
C11	0.828(1)	-0.0129(9)	0.8584(8)	1.0	0.032(2)
C12	0.929(1)	-0.1418(9)	0.8538(8)	1.0	0.032(2)
C13	1.062(1)	-0.1609(9)	0.8117(9)	1.0	0.033(2)
C14	1.099(1)	-0.0527(9)	0.7702(9)	1.0	0.034(2)

atom	U11	U22	U33	U23	U13	U12
Sb1	0.0243(5)	0.0216(5)	0.0281(5)	-0.0001(4)	0.0031(4)	-0.0035(4)
Cl1	0.026(1)	0.037(1)	0.040(1)	-0.006(1)	0.003(1)	-0.004(1)
Cl2	0.040(1)	0.027(1)	0.031(1)	0.008(1)	0.005(1)	-0.008(1)
Cl3	0.030(1)	0.028(1)	0.038(1)	-0.007(1)	0.002(1)	-0.005(1)
Sb2	0.0218(5)	0.0169(5)	0.0295(5)	-0.0024(4)	0.0021(4)	-0.0042(4)
Cl1X	0.051(2)	0.019(1)	0.057(2)	0.002(1)	-0.001(1)	-0.006(1)
Cl2X	0.053(3)	0.039(3)	0.110(4)	0.020(3)	-0.043(3)	-0.020(2)
Cl2Y	0.082(9)	0.040(6)	0.14(1)	-0.039(8)	0.094(9)	-0.033(7)
Cl3X	0.096(7)	0.042(3)	0.059(5)	-0.006(1)	0.051(4)	-0.009(5)
Cl3Y	0.102(7)	0.036(4)	0.078(6)	-0.013(4)	-0.063(5)	-0.009(4)
Br	0.0665(8)	0.0365(6)	0.0613(7)	-0.0003(5)	0.0168(6)	-0.0169(6)
N	0.036(5)	0.033(5)	0.040(5)	-0.007(4)	0.009(4)	-0.011(4)
O	0.041(4)	0.054(5)	0.046(4)	-0.001(4)	-0.001(3)	-0.013(4)

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

The crystals of **2b,g** consist of discrete $[C_{14}H_9BrNO]^+$ and $[C_{14}H_{10}NS]^+$ cations, respectively, and $SbCl_6^-$ anions. The unit cell of **2b** is centrosymmetric with the asymmetric unit containing one complete cation and two independent halves of $SbCl_6^-$ anions, the Sb atoms lying at inversion centers. The anion containing Sb2 as the central atom shows rotational disorder corresponding to two rotational positions related to each other by a rotation of about 20° around the axis Cl1X – Sb2 (Table 1). Refinement in space group *P*1 shows, that this is not due to a wrong choice of symmetry but is inherent to the structure.

Table 2. Fractional Atomic Coordinates and Temperature Parameters for **2g**[a)]

atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb	0.3425(2)	0.66470(9)	0.12976(6)	0.0414(6)	0.0380(6)	0.0420(6)	0.0006(6)	0.0231(5)	0.0036(6)
Cl1	0.4381(6)	0.5107(4)	0.1984(2)	0.074(3)	0.058(3)	0.060(3)	0.018(2)	0.039(2)	0.024(3)
Cl2	0.2464(7)	0.8196(4)	0.0595(3)	0.078(3)	0.050(3)	0.092(3)	0.024(3)	0.055(3)	0.024(3)
Cl3	0.0439(7)	0.6407(6)	0.1156(4)	0.063(4)	0.158(6)	0.168(6)	0.106(5)	0.079(4)	0.043(4)
Cl4	0.6432(7)	0.6873(5)	0.1424(4)	0.044(3)	0.101(5)	0.233(8)	0.070(5)	0.053(4)	0.000(3)
Cl5	0.276(1)	0.5666(4)	0.0294(3)	0.182(6)	0.058(3)	0.058(3)	-0.010(3)	0.062(4)	0.003(4)
Cl6	0.412(1)	0.7667(5)	0.2288(3)	0.30(1)	0.079(4)	0.064(4)	-0.026(4)	0.044(5)	0.053(6)
S	-0.2333(8)	0.4110(5)	0.1507(3)	0.088(4)	0.075(4)	0.087(4)	0.001(3)	0.054(3)	0.027(3)
N	0.031(2)	0.299(1)	0.1304(8)	0.05(1)	0.07(1)	0.07(1)	0.008(8)	0.026(9)	0.022(9)
C1	-0.089(2)	0.342(1)	0.1385(8)	0.07(1)	0.05(1)	0.028(9)	-0.010(9)	-0.006(8)	-0.01(1)
C2	0.084(2)	0.203(1)	0.1247(8)	0.06(1)	0.06(1)	0.033(9)	-0.001(8)	0.018(9)	0.04(1)
C3	0.218(2)	0.197(1)	0.0975(8)	0.03(1)	0.05(1)	0.04(1)	-0.015(8)	0.001(8)	0.003(8)
C4	0.321(2)	0.103(2)	0.1060(9)	0.05(1)	0.08(1)	0.05(1)	-0.01(1)	0.01(1)	0.02(1)
C5	0.439(3)	0.098(2)	0.076(1)	0.07(2)	0.09(2)	0.08(2)	-0.03(1)	0.03(1)	0.00(1)
C6	0.466(3)	0.183(2)	0.042(1)	0.07(1)	0.13(2)	0.15(2)	-0.04(2)	0.09(2)	0.01(2)
C7	0.371(3)	0.272(2)	0.034(1)	0.07(1)	0.10(2)	0.13(2)	-0.01(2)	0.07(2)	-0.01(1)
C8	0.245(2)	0.282(2)	0.061(1)	0.05(1)	0.06(1)	0.07(1)	-0.01(1)	0.03(1)	-0.01(1)
C9	0.009(2)	0.113(1)	0.1425(8)	0.05(1)	0.05(1)	0.04(1)	0.010(8)	0.016(9)	0.012(9)
C10	-0.047(3)	0.122(2)	0.1968(9)	0.09(1)	0.06(1)	0.04(1)	0.007(9)	0.04(1)	0.03(1)
C11	-0.128(3)	0.037(2)	0.211(1)	0.11(2)	0.09(2)	0.08(2)	0.03(1)	0.07(2)	0.05(2)
C12	-0.153(3)	-0.055(2)	0.177(1)	0.15(2)	0.08(2)	0.08(2)	0.02(1)	0.07(2)	0.04(2)
C13	-0.110(3)	-0.066(2)	0.122(1)	0.09(2)	0.06(1)	0.09(2)	0.01(1)	0.04(1)	0.02(1)
C14	-0.026(3)	0.017(1)	0.1061(9)	0.08(1)	0.04(1)	0.07(1)	0.01(1)	0.05(1)	0.01(1)

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a) The anisotropic temperature parameters are defined as in Table 1.

Table 3. Selected Bond Angles and Torsional Angles [°] for **2b** and **2g**

2b	O - C1 - N	172(1)	2g	S - C1 - N	173(2)
	C1 - N - C2	129.0(9)		C1 - N - C2	139(2)
	N - C2 - C3	115.3(9)		N - C2 - C3	115(2)
	N - C2 - C9	121.5(7)		N - C2 - C9	121(2)
	C2 - C3 - C4	122.1(8)		C2 - C9 - C10	119(2)
	C2 - C3 - C8	119.3(9)		C2 - C3 - C8	121(2)
	C2 - C9 - C10	119.8(7)		C2 - C3 - C4	120(2)
	C2 - C9 - C14	120.6(8)		C2 - C9 - C14	123(2)
	C1 - N - C2 - C3	+172.3(9)		S - C1 - N - C2	+170(10)
	C1 - N - C2 - C9	- 6(1)		C1 - N - C2 - C3	+165(2)
	N - C2 - C3 - C4	- 23(1)		C1 - N - C2 - C9	- 14(3)
	N - C2 - C3 - C8	+155.4(9)		N - C2 - C3 - C8	- 18(2)
	N - C2 - C9 - C10	+136.3(9)		N - C2 - C3 - C4	+163(1)
	N - C2 - C9 - C14	- 40(1)		N - C2 - C9 - C10	- 32(2)
	C3 - C2 - C9 - C10	- 42(1)		N - C2 - C9 - C14	+144(2)
	C3 - C2 - C9 - C14	+141.2(9)		C2 - C3 - C8 - C7	-178(2)
	C9 - C2 - C3 - C4	+156.0(9)		C2 - C9 - C10 - C11	+176(2)
	C9 - C2 - C3 - C8	- 26(1)		C9 - C2 - C3 - C8	+160(1)
	C2 - C3 - C4 - C5	180(1)		C3 - C2 - C9 - C10	+150(2)
	C2 - C9 - C14 - C13	+177.3(8)		C9 - C2 - C3 - C4	- 19(2)
				C3 - C2 - C9 - C14	- 35(2)

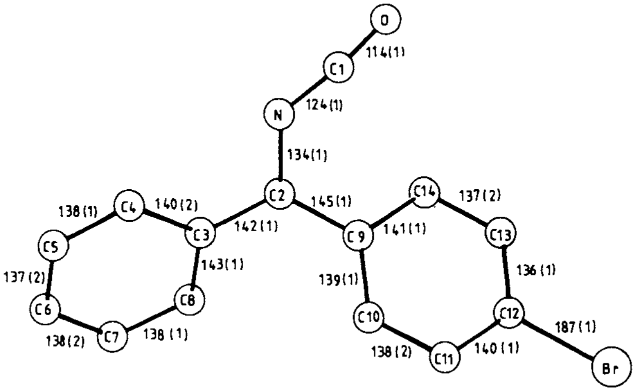


Fig. 1. Molecular Plot and Selected Bond Lengths [pm] for the Cation of **2b**

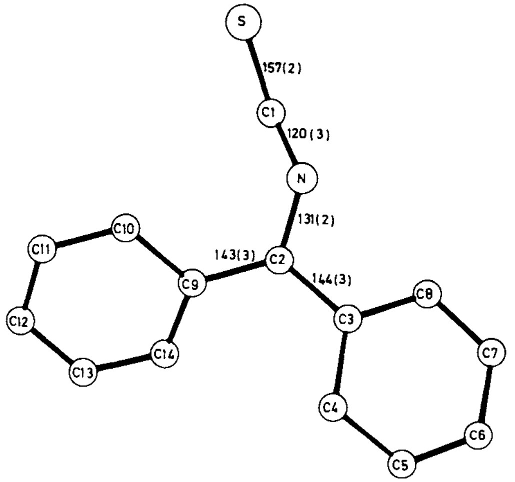
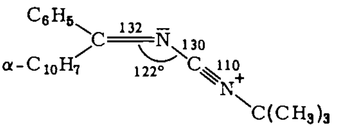
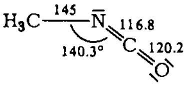


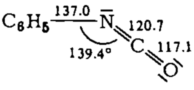
Fig. 2. Molecular Plot and Bond Lengths [pm] for the Cation of **2g**



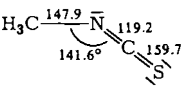
12 $SbCl_6^-$



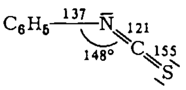
13



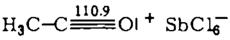
14



15

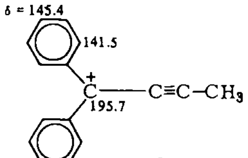


16



$H_3C-C\overset{110.9}{\equiv}O|^+ \; SbCl_6^-$

17



18

The observed geometrical parameters for **2b, g** may be compared with those of **12**[9] (*X*-ray diffraction), **13**[10] (electron diffraction), **14**[11] (microwave spectroscopy), **15**[10,12] (electron diffraction, microwave spectroscopy), **16**[13] (microwave spectroscopy), and **17**[14] (*X*-ray diffraction) (bond lengths in pm).

In **2b, g** the CNC units are bent (**2b**: 129°, **2g**: 139°). The bond angles are even smaller than those in **13** – **16**. Therefore, in the crystalline state, **2b, g** are pseudobutatrienes[15]. But the magnetic equivalence of the phenyl groups in **2a, g** at −10°C suggest that the C–N–C bending potentials are shallow. Should compounds **2** then be regarded as acylium salts **2″** ↔ **2‴**, in analogy to **12**? Typical acylium salts have $C\equiv\overset{+}{O}$ bond lengths of 111 pm[14], while for **13** and **14** C=O distances of 120.2 and 117.1 pm, respectively, have been reported[10,11]. For the cation of **2b** a C=O bond length of 114(1) pm has been found. The C2–N bond (134(1) pm) is only slightly longer than the C=N double bond in **12** (132 pm). These data suggest that all three canonical forms **2′** ↔ **2″** ↔ **2‴** contribute considerably to the structure of **2b**. Furthermore, the ^{13}C NMR data of **2a** remind of those of the 1,1-diphenyl-2-butinyl cation **18**[16] suggesting that in both cases the positive charge is delocalised to a certain degree into the aromatic rings. Similar conclusions may be drawn for **2g**. The observed C=S (157(2) pm) and N=C (120(3) pm) bond lengths are typical for aliphatic or aromatic isothiocyanates (**15**, **16**). Structures of thioacylium ions, which could be compared with **2g**, seem to be unknown[17]. The C2–N distance in **2g** (131(2) pm) and the corresponding distance in **12** are almost equal. Perhaps, for **2g** the contribution of the canonical forms **2″** ↔ **2‴** is somewhat less important than for **2a** reflecting the instability of a $C\equiv S^+$ triple bond as compared to a $C\equiv O^+$ triple bond.

It may be mentioned that in both **2b** and **2g** the NCX units stand almost eclipsed to one of the C–aryl bonds (**2b**: C1–N–C2–C9 −6(1)°, **2g**: C1–N–C2–C9 −14(3)°), thus maximizing conjugative effects between C=N and aryl. In both compounds the NCX units are not exactly linear (N–C1–O 172°, N–C1–S 173°), the X atom being turned away from the eclipsing aryl–C bond. According to recent *ab initio* calculations[18] the NCO group in HNCO is not linear showing a bond angle of 174°. The observed deviations from linearity of the NCX groups in **2b, g** may therefore be inherent properties of the molecules.

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Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer. – ^1H NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 instruments. – ^{13}C NMR spectra: Bruker WM-250 spectrometer, δ-scale, external reference tetramethylsilane in [D_6]acetone or internal reference tetramethylsilane. – The experiments were carried out under an atmosphere of argon. – The melting points are uncorrected.

4,4-Diphenyl-1-oxa-3-azabutatrienium Hexachloroantimonate (**2a**): To antimony pentachloride (0.30 g, 1.00 mmol, freshly distilled) was added at −20°C a solution of **1a**[1] (0.24 g, 1.00 mmol) in dry acetonitrile (3 ml). After 10 min the solvent was decanted from the yellow precipitate and fresh anhydrous acetonitrile (3 ml) was added. The mixture was allowed to warm to + 10°C at which temperature the precipitate dissolved giving a clear yellow solution. On cooling slowly to − 10°C **2a** fell out as large orange-brown prisms, which decomposed without melting above 100°C. – IR (CH_2Cl_2): **1a**: NCO 2239, C=O 1740 (vs), C=N 1620 cm^{-1}; **2a**: CNCO 2218, 1660, 1580 cm^{-1}. – ^{13}C NMR: **1a** (CD_3CN, 263 K): C=O δ = 171.1, C=N 156.3, aromatic C 135.6, 133.4, 130.4, 129.6, 129.4, 126.8; **2a** (CD_3CN, 263 K, TMS external): C=N 200.5, NCO 133.8, *i*-C 136.1, *o*-C 139.3, *m*-C 131.6, *p*-C 144.6.

4-(4-Bromophenyl)-4-phenyl-1-oxa-3-azabutatrienium Hexachloroantimonate (**2b**): As described for **2a** from **1b**$^{1)}$ (0.27 g, 1.00 mmol). Recrystallization from absol. acetonitrile at − 40°C afforded yellow-orange prisms. – ^{13}C NMR (CH_3CN, 263 K, TMS external): C=N δ = 205.4, NCO 133.6 (?).

4,4-Diphenyl-1-thia-3-azabutatrienium Hexachloroantimonate (**2g**)

a) From **1g**$^{4)}$ (0.26 g, 1.00 mmol) as described for **2a**. Recrystallization from absol. acetonitrile afforded orange prisms; m.p. 120 – 122°C (dec.). – IR (CH_2Cl_2): **1g**: NCS 2000 cm^{-1} (broad); **2g**: 1980, 1930, 1890 cm^{-1}. – ^{13}C NMR (CH_3CN, 263 K, TMS external): C=N δ = 194.8, NCS 135.0, *i*-C 136.7, *o*-C 138.7, *m*-C 131.3, *p*-C 143.7.

b) To **1g** (1.30 g, 5.00 mmol) in absol. dichloromethane (10 ml) was added at − 78°C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml). After warming to + 22°C absol. pentane (30 ml) was added dropwise affording an instable orange powder (2.54 g, 91%).

If a drop of water was added to a solution of this compound in acetonitrile, a brown-yellow precipitate soon fell out. In the ^{13}C NMR spectrum of the supernatant liquid only signals for benzophenone were observed: ^{13}C NMR (CH_3CN, TMS external): C=O δ = 197.2, aromatic C 138.2, 133.1, 130.3, 129.0.

(Diphenylmethylene)ammonium Hexachloroantimonate (**3a**)

a) To **1a** (1.22 g, 5.00 mmol) in absol. dichloromethane (10 ml) was added dropwise at − 78°C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml). After stirring for 30 min absol. ether (30 ml) was added dropwise. The yellow precipitate was filtered with exclusion of moisture and dried affording 2.52 g (93%) of **2a**. The yellow powder was suspended in dichloromethane (25 ml). After addition of water (0.11 g, 6.00 mmol) the mixture was stirred for 1 h at + 23°C. At − 25°C pale yellow prisms (1.94 g, 81%) crystallized; m.p. 195 – 196°C (dec.). – IR (CH_2Cl_2): C=N 1660 cm^{-1}. – ^{13}C NMR (CD_3CN): C=N δ = 185.9, *p,i*-C 137.6, 131.0, *o,m*-C 133.1, 130.4. – ^1H NMR (CD_3CN): NH δ = 10.25 (t, *J* = 56 Hz).

$[C_{13}H_{12}N]SbCl_6$ (516.7) Calcd. C 30.22 H 2.34 N 2.71 Found C 30.20 H 2.32 N 2.69

b) To **1a** (1.22 g, 5.00 mmol) in absol. dichloromethane (20 ml) was added dropwise at − 78°C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml) and then a solution of pivalic acid (1.03 g, 10.10 mmol) in absol. dichloromethane (10 ml). The mixture was stirred for 2 h at 22°C. Addition of pentane (40 ml) afforded **3a** as a pale yellow powder (2.53 g, 98%); m.p. 194 – 196°C (dec.). – The filtrate was evaporated under reduced pressure. Distillation of the oily residue gave pivalic anhydride (**4**) as a colourless oil (0.46 g, 49%); b.p. 74°C/13 Torr. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 27.0, C 38.7, C=O 185.5.

[(4-Bromophenyl)phenylmethylene]ammonium Hexachloroantimonate (**3b**): From **1b** (1.61 g, 5.00 mmol) as described for **3a**, b). Yield 2.77 g (93%) of a yellow powder, which was purified by stirring it for 30 min in dry dichloromethane (10 ml)/pentane (40 ml); m.p. 190 – 191°C. – IR (KBr): C=N 1650 cm^{-1}. – ^{13}C NMR (CH_3CN, TMS external): C=N δ = 184.1.

$[C_{13}H_{11}BrN]SbCl_6$ (595.6) Calcd. C 26.21 H 1.86 N 2.35 Found C 26.50 H 1.85 N 2.42

(1-Naphthylphenylmethylene)ammonium Hexachloroantimonate (**3c**): From **1c**$^{1)}$ (1.47 g, 5.00 mmol) as described for **3a**, b). Yield 2.69 g (95%) of orange crystals; m. p. 213 – 215 °C (dec.). – IR (KBr): C = N 1665 cm^{-1}. – ^{13}C NMR (CD$_3$CN): C = N δ = 186.3.

$[C_{17}H_{14}N]SbCl_6$ (566.8) Calcd. C 36.00 H 2.49 N 2.47 Found C 36.10 H 2.39 N 2.55

(2,2-Dimethyl-1-phenylpropylidene)ammonium Hexachloroantimonate (**3d**): From **1d**$^{1)}$ (1.12 g, 5.00 mmol) as described for **3a**, b). Yield after recrystallization from dichloromethane/pentane 2.24 g (90%) of a nearly colourless powder; m.p. 172 – 174 °C. – IR (KBr): C = N 1670 cm^{-1}. – ^{13}C NMR ([D$_6$]acetone): C = N δ = 203.8 (t, *J* = 9 Hz), CH$_3$ 27.8, C 42.3. – ^{1}H NMR ([D$_6$]acetone): CH$_3$ δ = 1.60, NH 12.19 (t, *J* = 63 Hz), 11.75 (t, *J* = 64 Hz).

$[C_{11}H_{16}N]SbCl_6$ (496.7) Calcd. C 26.60 H 3.25 N 2.84 Found C 26.38 H 3.18 N 2.84

The suspension of the yellow precipitate of **2d** [IR (CH$_2$Cl$_2$): CNCO 2235 cm^{-1}], which was formed from **1d** [IR (CH$_2$Cl$_2$): NCO 2246 cm^{-1}] and antimony pentachloride in dichloromethane, is unstable changing its colour within 5 min at 23 °C to white and later to dark brown.

9-Fluorenylideneammonium Hexachloroantimonate (**3e**): From **1e**$^{19)}$ (1.21 g, 5.00 mmol) as described for **3a**, b). Yield 2.44 g (95%) of a red-orange powder; m. p. 270 – 272 °C (dec.). – IR (KBr): 1695, 1675, 1600 cm^{-1}. – ^{13}C NMR (CD$_3$CN): C-9 δ = 178.7. – ^{1}H NMR (CD$_3$CN): NH δ = 10.46 (t, *J* = 47 Hz).

$[C_{13}H_{10}N]SbCl_6$ (514.7) Calcd. C 30.34 H 1.96 N 2.72 Found C 30.50 H 1.94 N 2.70

On addition of SbCl$_5$ to **1e** (IR (CH$_2$Cl$_2$): NCO 2240 cm^{-1}) in dichloromethane a dark green suspension of **2e** was obtained. – IR (CH$_2$Cl$_2$): CNCO 2215 cm^{-1}.

1-Oxo-3-phenyl-1H-benz[de]isoquinolinium Hexachloroantimonate (**5**): To **1c** (1.47 g, 5.00 mmol) (no NCO band in the IR spectrum in CH$_2$Cl$_2$. Only form **1'c** is present$^{2)}$) in absol. dichloromethane (5 ml) was added at – 78 °C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (5 ml). The dark violet suspension of **2c** [IR (CH$_2$Cl$_2$): CNCO 2205 cm^{-1} (vs)] was kept for 2 days at + 5 °C. During this time yellow-orange prisms of **5** crystallized (2.25 g, 76%), which were washed with pentane; m.p. 236 – 238 °C (dec.). – IR (KBr): 1690, 1580 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): NH δ = 8.97, CH – CH – CH 8.35 (d, *J* = 8 Hz), 7.74 (t, *J* = 8 Hz), 8.22 (d, *J* = 8 Hz), and 7.98 (d, *J* = 8 Hz), 7.56 (t, *J* = 8 Hz), 7.40 (d, *J* = 8 Hz).

$[C_{18}H_{12}NO]SbCl_6$ (592.8) Calcd. C 36.47 H 2.04 N 2.36 Found C 36.52 H 1.98 N 2.34

2,3-Dihydro-3-hydroxy-3-phenyl-1H-benz[de]isoquinolin-1-one (**6**)$^{3)}$: A solution of potassium hydroxide (2.80 g, 50.0 mmol) in water (40 ml) was added to **5** (2.96 g, 5.00 mmol) in dichloromethane (30 ml). After stirring for 12 h the product was filtered off. The aqueous layer of the filtrate was separated and extracted with dichloromethane (2 × 25 ml). The combined dichloromethane solutions were dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The combined products were washed with dichloromethane (30 ml)/pentane (20 ml) affording a pale yellow powder (1.21 g, 88%); m.p. 178 – 182 °C (dec.) (lit.$^{3)}$ 185 °C). – IR (CH$_2$Cl$_2$): 1660, 1575, 1530, NH 3380, OH 3560 cm^{-1}. – ^{13}C NMR ([D$_6$]DMSO): COH δ = 84.1, C = O 161.7. – ^{1}H NMR ([D$_6$]DMSO): OH δ = 3.40, NH 8.97.

[4-(Dimethylamino)phenyl]diphenylcarbenium Hexachloroantimonate (**8a**)

a) To **1a** (1.22 g, 5.00 mmol) in absol. dichloromethane (10 ml) was added at – 78 °C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml) and then a solution of *N,N*-dimethylaniline (0.61 g, 5.03 mmol) in absol. dichloromethane (10 ml). After stirring for 2 h at 23 °C and filtration dry pentane (50 ml) was added dropwise. Decanting of the solvent left a red oil, which after washing with pentane and drying gave an instable foam (2.92 g, 88%) of **7a**. – IR (CH$_2$Cl$_2$): NCO 2260 cm^{-1}. – ^{1}H NMR (CD$_2$Cl$_2$): CH$_3$ δ = 3.49 (d, *J* =

6.0 Hz), NH 9.15 (d, J = 6.0 Hz). – A solution of this foam in dry methanol (30 ml) was stirred for 1 h. Evaporation of the solvent afforded red crystals (2.43 g, 78%, relative to **1a**), which were washed with ether; m.p. 206 – 208 °C (dec.). – IR (CH_2Cl_2): 1610, 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 3.60. – ^{13}C NMR (CD_2Cl_2): carbenium C δ = 178.7, CH_3 43.0, eight aromatic C. – UV (CH_2Cl_2): λ_{max} 484 (log ε = 4.56), 357 (4.00), 267 nm (4.27).

$[C_{21}H_{20}N]SbCl_6$ (620.9) Calcd. C 40.62 H 3.25 N 2.26 Found C 40.70 H 3.18 N 2.32

b) From **1g** (1.30 g, 5.00 mmol) as described in a). Yield 2.45 g (79%) of red crystals; m.p. 204 – 206 °C (dec.).

9-[4-(Dimethylamino)phenyl]-9-fluorenium Hexachloroantimonate (**8e**): The intermediate **7e** was prepared from **1e** (1.21 g, 5.00 mmol) as described for **8a**, a). Yield 3.18 g (96%) of a brown powder. – IR (CH_2Cl_2): NCO 2240 cm^{-1} (vs). Stirring the solution of **7e** in dichloromethane (15 ml)/methanol (10 ml) for 30 min and evaporation of the solvent afforded an oil, which crystallized at –25 °C from dichloromethane (10 ml)/pentane (50 ml) yielding violet prisms (2.12 g, 69%); m.p. 200 – 202 °C. – IR (CH_2Cl_2): 1600 cm^{-1}. – UV (CH_2Cl_2): λ_{max} 545 (log ε = 4.50), 422 (3.94), 400 (3.75), 366 (3.39), 328 (3.79), 270 nm (4.54). – ^{13}C NMR of **9e** (from **8e** in [D_6]DMSO + 1 drop of H_2O): CH_3 δ = 45.6, COH 82.1, 10 aromatic C.

$[C_{21}H_{18}N]SbCl_6$ (618.8) Calcd. C 40.76 H 2.93 N 2.26 Found C 40.70 H 2.82 N 2.32

Antimony Pentachloride-1-(1-Cyclohexen-1-yl)pyrrolidine (**11**): To **1a** (0.61 g, 2.50 mmol) in absol. dichloromethane (5 ml) was added at –78 °C a solution of antimony pentachloride (0.75 g, 2.50 mmol) in absol. dichloromethane (5 ml) and then a solution of **10** (0.38 g, 2.50 mmol) in absol. dichloromethane (5 ml). After stirring for 2 h at +23 °C absol. pentane (10 ml) was added. At –25 °C colourless prisms (0.83 g, 74%) of **11** crystallized; m.p. 121 – 122 °C (dec.). – IR (CH_2Cl_2): 1655 cm^{-1}.

$C_{10}H_{17}N \cdot SbCl_5$ (450.3) Calcd. C 26.67 H 3.81 N 3.11 Found C 27.17 H 3.69 N 3.22

Evaporation of the filtrate yielded a foam (0.77 g), which contained **1a**. – IR (CH_2Cl_2): NCO 2239 cm^{-1}.

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