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# Amino-substituted 2-Azaallenium Salts

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Nitrilium salts (**14a – i**) react with imines (**15a – e**) to afford the mono- to tetraaza-substituted 2-azaallenium salts **16a – w** in high yields. The stereochemistry of these compounds is discussed in terms of an allenic geometry (**A**) and a planar 1,3-diaza-1,3-butadienium structure (**B**), respectively. According to the IR, $^1$H and $^{13}$C NMR spectra, the azaallenium salts **16** are rather flexible around the central nitrogen atom. In solution at least **16a – d** assume chiral conformations similar to those of allenes. By DNMR measurements barriers to hindered rotation around the C=$\overset{+}{\text{N}}$=C axis were found to range from $\Delta G^{\ddagger}_{173}$ = 36 ± 1 kJmol$^{-1}$ for **16a** to more than 90 kJmol$^{-1}$ for **16c**. According to an X-ray structural analysis, **16o** crystallizes in an almost perfect allene geometry (**A**). – Some interesting $^{13}$C-$^{14}$N couplings of the nitrilium salts **14** are reported.

**Aminosubstituierte 2-Azaalleniumsalze**

Nitriliumsalze (**14a – i**) reagieren mit Iminen (**15a – e**) in guten Ausbeuten zu den mono- bis tetraazasubstituierten 2-Azaalleniumsalzen **16a – w**. Für die Verbindungen **16** wird eine Allengeometrie (**A**) oder alternativ eine planare 1,3-Diaza-1,3-butadienium-Struktur (**B**) diskutiert. Nach den IR-, $^1$H- und $^{13}$C-NMR-Spektren zu schließen, müssen die Salze **16** um das zentrale Stickstoffatom recht flexibel sein. Zumindest die Verbindungen **16a – d** liegen in Lösung in einer chiralen Allenkonformation vor. Für die Rotationsbarrieren um die C=$\overset{+}{\text{N}}$=C-Achse werden durch DNMR-Messungen Werte zwischen $\Delta G^{\ddagger}_{173}$ = 36 ± 1 kJmol$^{-1}$ für **16a** und mehr als 90 kJmol$^{-1}$ für **16c** gefunden. Nach einer Röntgenstrukturanalyse liegt **16o** im Kristall in einer weitgehend idealen Allengeometrie (**A**) vor. – Es werden einige interessante $^{13}$C-$^{14}$N-Kopplungen der Nitriliumsalze **14** beschrieben.

While the chemistry of allenes is well developed[1], little is known about the 2-aza analogs of allenes, the 2-azaallenium salts **2**.

To our knowledge *Samuel* and *Wade* in 1969 prepared the first 2-azaallenium salts (**2**) by chloride abstraction from *N*-chloromethyl imines **1** with Lewis acids, e.g. antimony pentachloride[2]. These authors assigned a moderately strong broad IR absorption over the range of 1820 – 1870 cm$^{-1}$ to an asymmetric skeletal stretching vibration of the presumably linear C=$\overset{+}{\text{N}}$=C moiety. *Barton* et al.[3,4] prepared a few compounds **2** from *N*-methylimines **3** by hydride abstraction with the help of triarylcarbenium ions.

Recently, a third method for the synthesis of compounds **2** has been described by *Würthwein*[5] who reacted the iminals **4** with acylium salts. According to MNDO and ab initio calculations[6] and the IR spectra, the carbon-substituted 2-azaallenium salts **2** must be regarded as true cumulenes with a linear $\rangle$C=$\overset{+}{\text{N}}$=C$\langle$ skeleton of $D_{2d}$ symmetry.

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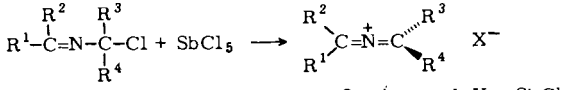
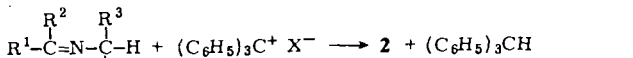
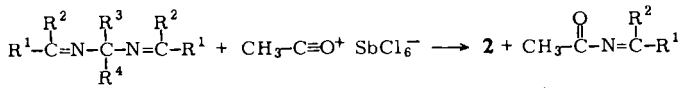


**1** **2**: $R^i$ = aryl, X = $SbCl_6$

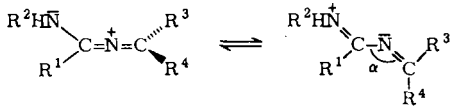


**3** $R^i$ = aryl or $R^1 = R^2 = H, R^3 = R^4$ = aryl



**4** X = $SbCl_6$, $R^i$ = aryl or $R^1 = R^2 = H, R^3 = R^4$ = aryl

Less clear is the stereochemistry of heterosubstituted formal 2-azaallenium salts. In the case of an azasubstituted 2-azaallenium cation qualitative valence bond theory suggests the possibility of two valence tautomeric structures **A** and **B**.



**A**: $\beta = 90°$ **B**: $\beta = 0°$

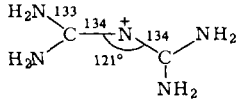
$\beta$: angle between the planes through $NR^1CN$ and $R^3R^4CN$

Form **A** has allene geometry with a linear $C=\overset{+}{N}=C$ moiety and planes through $NR^1CN$ and $R^3R^4CN$ which are perpendicular with respect to one another ($\beta = 90°$). Form **B** should have a planar molecular frame. The central CNC unit is bent by approximately $\alpha = 120°$. In form **B** the lone pair of electrons of the central nitrogen atom is orthogonal to the $\pi$ system. The IR spectra should show absorptions for the C=N stretching vibrations below 1700 $cm^{-1}$ while for **A** a band for the asymmetric C=N=C stretching vibration above 1800 $cm^{-1}$ is to be expected. If there are more than one aza substituents, several canonical forms of **B** must be considered in all of which the lone pair of electrons at the central nitrogen atom is not involved in conjugation.

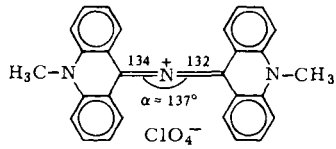
An old example of a tetraaza-substituted formal 2-azaallenium salt is the monoprotonated biguanide **5** which has first been obtained by *Rathke*[7] from dicyandiamide and ammonia.

X-ray structural analyses[8-10] of monoprotonated biguanides reveal that these molecules crystallize with geometries intermediate to those expected for **A** or **B**. The CNC bond angle is 121° as predicted for form **B**. But while the unprotonated biguanide is almost planar, the monocation consists of two planar NNCN halves which are twisted with respect to one another by 40–50° depending on the counterion. This is half of the value expected for **A**. Vinylogous to a tetraaza-substituted 2-azaallenium salt is the dyestuff **6**. The compound shows a geometry similar to that of form **A** ($\alpha = 137°$, $\beta = 66°$)[11]. The deviation from planarity has been attributed to sterical interactions. Apparently, the possibility of a structure with cumulated double bonds has not been considered.

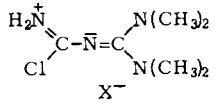
The IR spectra of the chlorotriaza-substituted formal 2-azaallenium salts **7** and of similar compounds have been interpreted in terms of form **B** only[12,13]. Strong absorptions at 1646 and 1633 $cm^{-1}$ were assigned to stretching vibrations of the central and the peripheral C=N double bonds. On the other hand, for the tetrachloro compound **8** an allenic structure in analogy to **A** has been postulated[14]. The salt shows a strong IR absorption at 1855 $cm^{-1}$.



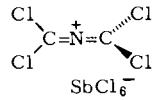

**5**[10]; $\beta$ = 40-50°



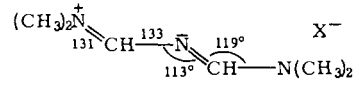

**6**[11]; $\beta$ = 66°




**7**



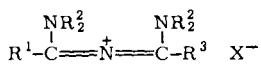

**8**



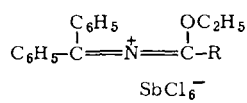

**9**: X = $I_3$[18]

Compound **9** known as *Gold's* reagent[15], which is easily prepared from cyanuric trichloride or dichlorophosphazene with dimethylformamide[16,17], can be regarded as a formal 1,3-diaza-substituted 2-azaallenium salt. For the chloride **9** $\nu_{C=N}$ = 1600 $cm^{-1}$ was reported[15]. According to an X-ray structural analysis[18] of the triiodide (**9**, X = $I_3$), the central bond angle $\alpha$ = 113° is very small. All the carbon and nitrogen atoms seem to be lying in one plane. There is no doubt therefore that the cation **9** has the structural features of form **B** only. Recently, *Gold's* reagent has found interesting synthetic applications[19-21].

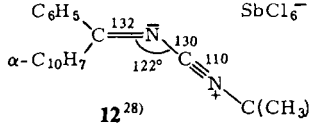
Several tri- and tetrahetero-substituted formal 2-azaallenium salts (**10**) have been prepared by *Gompper* et al.[22]. In this and similar cases[23-26] little has been reported concerning the structure of the products.



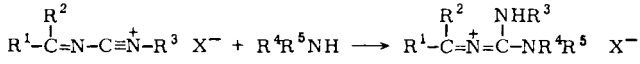

**10**




**11**




**12**[28]

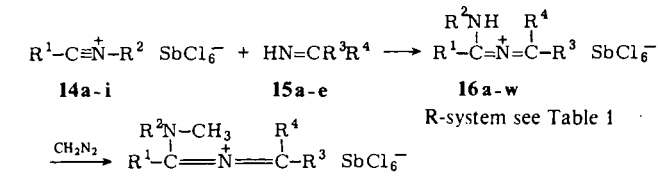



**13**

Quite recently, *Würthwein* et al. reported on the synthesis of the first monooxa-substituted 2-azaallenium ions **11**[27]. Compounds **11** show strong IR absorption at 1695 – 1700 $cm^{-1}$. This and the $^{13}C$ NMR spectra were interpreted to be in agreement with a 2-azaallenium structure.

In the course of our search for new heterocumules we obtained some formal 1,3-diazabutatrienium salts which can also be regarded as heterosubstituted 2-azaallenium compounds[28,29]. An X-ray structural analysis of **12** revealed the bent structure of an alkylidenecyanamidium salt ($\alpha$ = 122°). These salts react with primary and secondary amines to give the formal 2-azaallenium salts **13** which exhibit absorptions for the C=N double bonds in the range of 1550 to 1690 $cm^{-1}$[30].

In this paper we report a new and general method for the preparation of mono- to tetraaza-substituted 2-azaallenium salts **16**.




| 14 | $R^1$ | $R^2$ |
|---|---|---|
| a | $CH_3$ | $(CH_3)_2CH$ |
| b | $(CH_3)_2CH$ | $(CH_3)_2CH$ |
| c | $(CH_3)_3C$ | $(CH_3)_2CH$ |
| d | $C_6H_5$ | $(CH_3)_2CH$ |
| e | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ |
| f | $(CH_3)_2CH(CH_3)N$ | $(CH_3)_2CH$ |
| g | $(CH_3)_2N$ | $(CH_3)_3C$ |
| h | $[(CH_3)_2CH]_2N$ | $(CH_3)_2CH$ |
| i | $[(CH_3)_2CH]_2N$ | $CH_3$ |

| 15 | $R^3$ | $R^4$ |
|---|---|---|
| a | $C_6H_5$ | $C_6H_5$ |
| b | $C_6H_5$ | $(CH_3)_3C$ |
| c | $(CH_3)_3C$ | $(CH_3)_3C$ |
| d | $o\text{-}C_6H_4\text{–}C_6H_4\text{-}o'$ | |
| e | $(CH_3)_2N$ | $(CH_3)_2N$ |

Nitrilium and cyanamidium salts **14** readily react at low temperature with imines **15** to give the compounds **16a–w** in high yields. Reaction of **16d** with diazomethane resulted in the formation of **16x**.

The IR spectra of most of the salts **16** show two strong bands in the range of 1500 to 1825 $cm^{-1}$ which may be assigned to C=N stretching vibrations (Table 1. Additional weaker bands and shoulders are not included in the Table). As can be seem from Table 1 the position of the band with the higher wave number varies from 1550 to 1825 $cm^{-1}$, while the low frequency band has the narrower range of 1510 to 1615 $cm^{-1}$. With increasing wave number of the first band its intensity and line width increases, while the wave number, intensity and line width of the second band decreases. For tetraphenyl-2-azaallenium hexachloroantimonate a cumulene band at 1870 $cm^{-1}$ has been reported[5]. Compound **16o** shows a broad and intensive band at 1825 $cm^{-1}$ suggesting that this salt has the allene topology of form **A**. According to the data of Table 1, the geometry of **16** is determined by the steric requirements of its substituents. Bulky *tert*-butyl groups favour geometry **A**. An increasing number of aza substituents stabilizes form **B**.

These conclusions are corroborated by NMR data and an X-ray diffraction analysis of **16o**.

In the $^1H$ and $^{13}C$ NMR spectra for **16c** at room temperature the signals for the isopropyl methyl groups appear doubled. Since none of the other signals of **16c** shows any doubling and since this doubling is not observed for **16o**, the isopropyl groups of **16c** must be diastereotopic, contrary to those of **16o**. This is just what one expects for compounds **16** with the topology of form **A**. With unequal substituents on each end of the C=N=C moiety compounds **16** are chiral.

With increasing temperature the $^1H$ shift difference of the diastereotopic methyl groups of **16c** decreases and disappears above 335 K ($CDCl_3$, 250 MHz). On the other hand, the $^{13}C$ resonances show little temperature dependence. Up to 373 K the $^{13}C$ signals for the diastereotopic methyl groups remain sharp (in [$D_5$]bromobenzene, external reference cyclosilane, $CH_3$ $\delta$ = 17.8, 17.3, $\Delta\nu$ = 29 Hz). At higher temperatures the compound decomposes quickly. Therefore, only a lower limit of $\Delta G^{\neq}_{373} > 90\,kJmol^{-1}$ can be given for the barrier to racemization of **16c**. This barrier ensures sufficient sterical stability of the enantiomers for an optical resolution of **16c** at room temperature.

Table 1. Position of the Two Strong IR Absorptions Between 1500 and 1825 $cm^{-1}$ of the Compounds **16**

| 16 | $R^1$ | $R^2$ | $R^3$ | $R^4$ | C=N ($CH_2Cl_2$) $cm^{-1}$ |
|---|---|---|---|---|---|
| a | $CH_3$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1675, 1615 |
| b | $(CH_3)_2CH$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1700, 1595 |
| c | $(CH_3)_3C$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1710, 1575 |
| d | $C_6H_5$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1670, 1595 |
| e | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ | $C_6H_5$ | $(CH_3)_3C$ | 1650, 1580 |
| f | $CH_3NCH(CH_3)_2$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1640, 1600 |
| g | $(CH_3)_2CH$ | $(CH_3)_2CH$ | $C_6H_5$ | $C_6H_5$ | 1675, 1590 |
| h | $(CH_3)_3C$ | $(CH_3)_2CH$ | $C_6H_5$ | $C_6H_5$ | 1680, 1580 |
| i | $C_6H_5$ | $(CH_3)_2CH$ | $C_6H_5$ | $C_6H_5$ | 1645, 1585 |
| j | $(CH_3)_2N$ | $(CH_3)_3C$ | $C_6H_5$ | $C_6H_5$ | 1625, 1600 |
| k | $[(CH_3)_2CH]_2N$ | $(CH_3)_2CH$ | $C_6H_5$ | $C_6H_5$ | 1620, 1590 |
| l | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ | $C_6H_5$ | $C_6H_5$ | 1625, 1580 |
| m | $C_6H_5$ | $(CH_3)_2CH$ | o-$C_6H_4$-$C_6H_4$-o' | | 1690, 1600 |
| n | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ | o-$C_6H_4$-$C_6H_4$-o' | | 1670, 1580 |
| o | $(CH_3)_3C$ | $(CH_3)_2CH$ | $(CH_3)_3C$ | $(CH_3)_3C$ | 1825, 1535 |
| p | $C_6H_5$ | $(CH_3)_2CH$ | $(CH_3)_3C$ | $(CH_3)_3C$ | 1775, 1540 |
| q | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ | $(CH_3)_3C$ | $(CH_3)_3C$ | 1690, 1555 |
| r | $(CH_3)_3C$ | $(CH_3)_2CH$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1630, 1560, 1530, 1510 |
| s | $C_6H_5$ | $(CH_3)_2CH$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1585, 1540, 1515 |
| t | $[(CH_3)_2CH]_2N$ | $(CH_3)_3C$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1560 |
| u | $(CH_3)_2N$ | $(CH_3)_3C$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1575, 1520 |
| v | $[(CH_3)_2CH]_2N$ | $(CH_3)_2CH$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1550 |
| w | $[(CH_3)_2CH]_2N$ | $CH_3$ | $(CH_3)_2N$ | $(CH_3)_2N$ | 1570, 1520 |
| x | $C_6H_5$ | $(CH_3)_2CH$ | $C_6H_5$ | $(CH_3)_3C$ | 1665, 1640 |

Enhanced flexibility around the central nitrogen atom is observed for **16a, b, d**. At low temperatures two lines for the isopropyl methyl groups of **16d** are observed in the $^{13}C$ NMR spectrum ($CD_2Cl_2$, 223 K, $CH_3$ $\delta$ = 21.9, 21.1, $\Delta\nu$ = 49 Hz). From the coalescence at 255 K of these signals a barrier to racemization of $\Delta G^{\ddagger}_{255} = 52 \pm 1$ kJmol$^{-1}$ was calculated. Again, compound **16p** with two equal (and magnetically equivalent) substituents on one end of the azaallenium unit does not show any splitting of the isopropyl methyl signals at low temperature, thus confirming that the observed dynamic effect for **16d** is really a hindered rotation around the C=N=C axis. Similarly, barriers to racemization of **16a** ($\Delta G^{\ddagger}_{173}$ = 36 kJmol$^{-1}$, $T_c$ = 173 K, $\Delta\nu$ = 22 Hz) and **16b** (*N*-isopropyl: $\Delta G^{\ddagger}_{246}$ = 50 kJmol$^{-1}$, $T_c$ = 246 K, $\Delta\nu$ = 49 Hz; *C*-isopropyl: $\Delta G^{\ddagger}_{243}$ = 50 kJmol$^{-1}$, $T_c$ = 243 K, $\Delta\nu$ = 33.5 Hz) have been determined.

Dynamic effects of a different kind, namely hindered rotation around the NC=N partial double bonds, can be observed for the polyaza-substituted salts **16**. Barriers corresponding to this process, which in some cases amount to more than 100 kJmol$^{-1}$, will be reported elsewhere.

Finally, the NMR spectra of some of the nitrilium salts **14** seem worth mentioning. To our knowledge $^{13}C$ NMR spectra of nitrilium salts have not been published[31-33]. In the broad band proton decoupled $^{13}C$ NMR spectrum of **14a** the signal for the nitrilium carbon is split into a well resolved triplet due to a $^{13}C$-$^{14}N$ coupling ($CD_3CN$, 263 K, $\delta$ = 109.3, t, $J$ = 43.1 Hz). Also, the $^{13}CH$ resonance appears as a triplet ($\delta$ = 53.8, t, $J$ = 3.5 Hz), while the methyl carbons ($\delta$ = 5.1, 21.0) form singlets. In the $^1H$ NMR spectrum of **14a** the signal for the isopropyl methyl groups ($CD_3CN$, 263 K, $\delta$ = 1.56) consists of five lines which may be interpreted as arising from a $^3J_{H,^{14}N}$ coupling of 2.4 Hz and a $^3J_{HH}$ coupling of 6.7 Hz. The methyl signal at $\delta$ = 2.81 is split into a doublet with broad lines due to a $^4J_{HH}$ coupling of 1.8 Hz and other unresolved long range couplings. Similar, for **14b** ($CD_2Cl_2$, 269 K, $^{13}C\equiv N$ $\delta$ = 112.6) a well resolved $^{13}C$-$^{14}N$ coupling of 38.4 Hz and a $^5J_{HH}$ coupling of 1.8 Hz have been observed. The unresolved $^3J_{H,^{14}N}$ coupling causes line broadening. $^{13}C$-$^{14}N$ couplings were observed for **14c, d** but not for any of the cyanamidium salts **15**.

## X-Ray Diffraction Analysis of 16o

A list of atomic coordinates with LS-computed standard deviations is given in Table 2. In Table 3 selected bond angles and torsional angles of **16o** are listed. Fig. 1 shows a molecular plot and bond lengths of the cation **16o**.

The crystals of **16o** consist of discrete $[C_{17}H_{35}N_2]^+$ cations and $SbCl_6^-$ anions. The C9 – N1 – C1 unit is not completely linear as expected for form **A** but the bond angle is large ($\alpha$ = 156°). The bond lengths C9 – N1 (127 pm) and N1 – C1 (128 pm) are shorter than those found in **5, 6, 9** or **12** indicating an increased double bond character in **16o**. Correspondingly, the C1 – N2 bond is somewhat longer (133 pm) than the comparable bond in **9** (131 pm). C – N bond lengths of about 133 pm are typically found in amides (e.g. oxamide 132 pm[34]), while C – N single bonds are longer (e.g. trimethylamine 147 pm[34]). Thus, the C1 – N2 bond in **16o** has still considerable double bond character as expected for form **B**. Atoms C9 and C1 lie slightly (8 and 5 pm) outside the planes through N1, C10, C14 and N1, N2, C2, respectively. Therefore, the dihedral angle be-

tween the planes through the molecular halves is not well defined. Nevertheless, the torsional angle C10 – C9 – C1 – C2 of −93° is that expected for an allene **A**.

Table 2. Fractional Atomic Coordinates and Temperature Parameters of **16o** [a]

| atom | x/a | y/b | z/c | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|---|---|---|
| Sb | 0.30636(8) | 0.67113(8) | 0.76166(6) | 0.0309(5) | 0.0245(4) | 0.0360(5) | 0.0073(3) | 0.0159(4) | 0.0086(3) |
| C11 | 0.1219(3) | 0.6671(4) | 0.8262(3) | 0.035(2) | 0.067(2) | 0.052(2) | 0.018(2) | 0.022(2) | 0.004(2) |
| C12 | 0.4196(4) | 0.5426(4) | 0.8720(3) | 0.083(3) | 0.064(2) | 0.083(3) | 0.047(2) | 0.043(2) | 0.045(2) |
| C13 | 0.1798(5) | 0.4754(4) | 0.6207(3) | 0.115(4) | 0.048(2) | 0.060(3) | -0.019(2) | 0.033(3) | -0.016(2) |
| C14 | 0.4881(4) | 0.6832(4) | 0.6962(4) | 0.067(3) | 0.079(3) | 0.099(3) | 0.045(2) | 0.064(2) | 0.044(2) |
| C15 | 0.1948(4) | 0.8070(4) | 0.6541(3) | 0.055(2) | 0.067(2) | 0.050(2) | 0.031(2) | 0.027(2) | 0.036(2) |
| C16 | 0.4298(4) | 0.8700(3) | 0.9024(3) | 0.050(2) | 0.041(2) | 0.051(2) | -0.001(2) | 0.012(2) | -0.008(2) |
| N1 | 0.8656(9) | 0.1698(9) | 0.7416(7) | 0.024(5) | 0.027(5) | 0.038(6) | 0.014(4) | 0.011(4) | 0.014(4) |
| N2 | 0.950(1) | -0.0251(9) | 0.7189(8) | 0.026(6) | 0.035(6) | 0.042(6) | 0.002(5) | 0.004(5) | 0.009(5) |

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| C1 | 0.9632(8) | 0.1038(9) | 0.7721(7) | C2 | 1.1078(7) | 0.1752(7) | 0.8605(5) |
| C3 | 1.099(1) | 0.3164(9) | 0.9206(9) | C4 | 1.216(1) | 0.188(1) | 0.8093(9) |
| C5 | 1.153(1) | 0.092(1) | 0.9397(8) | C6 | 0.824(1) | -0.106(1) | 0.624(1) |
| C7 | 0.800(1) | -0.249(1) | 0.630(1) | C8 | 0.842(2) | -0.101(1) | 0.521(1) |
| C9 | 0.7543(8) | 0.2141(7) | 0.7383(6) | C10 | 0.6725(7) | 0.1732(7) | 0.8033(6) |
| C11 | 0.750(1) | 0.085(1) | 0.8685(9) | C12 | 0.5245(9) | 0.093(1) | 0.7265(9) |
| C13 | 0.660(1) | 0.300(1) | 0.8802(9) | C14 | 0.7250(8) | 0.3258(8) | 0.6836(6) |
| C15 | 0.814(1) | 0.329(1) | 0.615(1) | C16 | 0.5681(9) | 0.301(1) | 0.6133(9) |
| C17 | 0.766(1) | 0.4634(8) | 0.7707(9) | | | | |

| atom | U | atom | U | atom | U | atom | U |
|---|---|---|---|---|---|---|---|
| C1 | 0.027(3) | C2 | 0.033(3) | C3 | 0.079(2) | C4 | 0.079(2) |
| C5 | 0.079(2) | C6 | 0.043(3) | C7 | 0.054(4) | C8 | 0.056(4) |
| C9 | 0.024(3) | C10 | 0.040(3) | C11 | 0.079(2) | C12 | 0.079(2) |
| C13 | 0.079(2) | C14 | 0.077(5) | C15 | 0.079(2) | C16 | 0.079(2) |
| C17 | 0.079(2) | | | | | | |

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

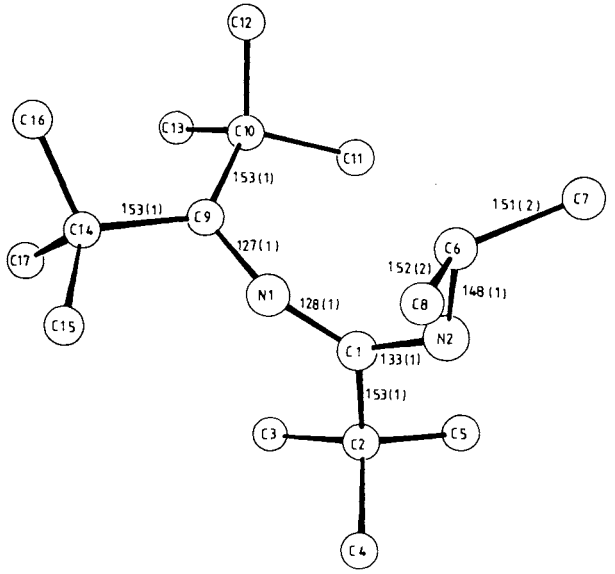



Fig. 1. Molecular Plot and Bond Lengths for the Cation **16o**

Table 3. Selected Bond Angles and Torsional Angles [°] of **16o**

| | | | |
|---|---|---|---|
| C9 - N1 - C1 | 156(1) | C14 - C9 - C1 - N2 | -111(1) |
| N1 - C1 - N2 | 121(1) | C2 - C1 - N2 - C6 | -173(1) |
| N1 - C1 - C2 | 121(1) | C1 - N2 - C6 - C7 | -142(1) |
| C10 - C9 - N1 | 120(1) | C3 - C2 - C1 - N2 | -174(1) |
| C14 - C9 - N1 | 116(1) | C3 - C2 - C1 - N1 | + 15(1) |
| N2 - C6 - C8 | 111(1) | C11 - C10 - C9 - N1 | + 3(1) |
| N2 - C6 - C7 | 109(1) | C11 - C10 - C9 - C14 | -166(1) |
| C10 - C9 - C1 - C2 | - 93(1) | C15 - C14 - C9 - N1 | + 17(1) |
| C10 - C9 - C1 - N2 | + 81(1) | C15 - C14 - C9 - C10 | -174(1) |
| C14 - C9 - C1 - C2 | + 75(1) | | |

In conclusion, these data show that aza-substituted 2-azaallenium salts are rather flexible around the central nitrogen atom (N1 in **16o**). In form **A** sterical interactions between the substituents on different ends of the $C=\overset{+}{N}=C$ unit are minimized. Electronically form **B** seems to be preferred. The shape of the real molecule is a result of a compromise between sterical and electronical requirements of the substituents, but not of the stiffness of the 2-azaallenium unit itself.

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## Experimental Part

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

*N-Isopropylacetonitrilium hexachloroantimonate* (**14a**)[35]: To acetonitrile (2.05 g, 50 mmol) in dry dichloromethane (80 ml) was added at – 78 °C a solution of antimony pentachloride (14.95 g, 50 mmol) in dry dichloromethane (20 ml). After stirring for 20 min at – 78 °C and then for 30 min at 0 °C the mixture was cooled to – 50 °C. The acetonitrile-antimony pentachloride complex was precipitated by slow addition of dry pentane (200 ml). After filtration with exclusion of moisture the complex was stirred in dry isopropyl chloride (70 ml) at + 22 °C for 12 h. The colourless moisture-sensitive precipitate (17.16 g, 82%) was collected and washed with dry pentane; m.p. 122 – 124 °C. – $^1H$ NMR ($CD_3CN$, 263 K): $CH_3$ δ = 1.56 (m, $^3J_{HH}$ = 6.7 Hz, $^3J_{H,^{14}N}$ = 2.4 Hz), 2.81 (d, $^4J_{HH}$ = 1.8 Hz), CH 4.58 (m, broad). – $^{13}C$ NMR ($CD_3CN$, 263 K): $CH_3$ δ = 5.1, $(CH_3)_2$ 21.0, CH 53.8 (t, $^1J_{^{13}C,^{14}N}$ = 3.5 Hz), C≡N 109.3 (t, $^1J_{^{13}C,^{14}N}$ = 43.1 Hz).

*N-Isopropylisobutyronitrilium hexachloroantimonate* (**14b**): From isobutyronitrile (3.46 g, 50 mmol) as described for **14a**. The product was precipitated at – 50 °C by addition of dry ether (200 ml) affording a colourless moisture-sensitive powder (17.20 g, 77%); m.p. 125 – 127 °C. – $^1H$ NMR ($CD_2Cl_2$): $CH_3$ δ = 1.71 (d, $J$ = 7.0 Hz), 1.75 (d, broad, $J$ = 6.7 Hz), CH 3.80 (m, $^2J_{HH}$ = 7.0 Hz, $^5J_{HH}$ = 1.8 Hz), 4.79 (m, $^2J_{HH}$ = 6.7 Hz, $^5J_{HH}$ = 1.8 Hz). – $^{13}C$ NMR ($CD_2Cl_2$, 269 K): $CH_3$ δ = 18.4, 21.6 or 21.9, CH 21.9 or 21.6, 55.0, C≡N 112.6 (t, $J$ = 38.4 Hz). – IR ($CH_2Cl_2$): C≡N 2330 $cm^{-1}$.

*N-Isopropyl-2,2-dimethylpropionitrilium hexachloroantimonate* (**14c**): From pivalonitrile (4.16 g, 50 mmol) as described for **14b**. Yield 17.28 g (75%) of a colourless powder; m.p.

133 – 135 °C. – $^1$H NMR ($CD_2Cl_2$, 263 K): $CH_3$ δ = 1.74, 1.74 (d, $J$ = 6.6 Hz), CH 4.85 (sept, $J$ = 6.6 Hz). – $^{13}$C NMR ($CD_2Cl_2$, 263 K): $CH_3$ δ = 21.1, 26.7, C 30.2, CH 54.7, C≡N 113.2 (t, broad, $J_{^{13}C,^{14}N} \approx 36$ Hz). – IR ($CH_2Cl_2$): C≡N 2340 cm$^{-1}$ (shoulder 2300).

$[C_8H_{16}N]SbCl_6$ (460.7) Calc. C 20.85 H 3.50 N 3.04 Found C 20.29 H 3.63 N 2.89

*2-Azaallenium hexachloroantimonates* (**16**)

*General procedure:* To 10 mmol of the nitrilium salt **14** in 10 ml of dry dichloromethane was added dropwise with stirring at – 78 °C a solution of 10 mmol of the imine **15** in dry dichloromethane (10 ml). Stirring was continued for 20 min at – 78 °C and then for 1 h at + 22 °C. After cooling to – 50 °C the product was precipitated by slow addition of dry ether (100 ml). Reprecipitation from dichloromethane (10 ml)/ether (80 ml) at – 50 °C afforded the pure product.

*1-tert-Butyl-3-(isopropylamino)-3-methyl-1-phenyl-2-azaallenium hexachloroantimonate* (**16a**): From **14a** (4.19 g) and **15b**[36,37] (1.61 g). Yield 5.05 g (87%) of a colourless powder which slowly decomposes in solution; m.p. 120 – 125 °C. – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.36, 1.43 (d, $J$ = 6.8 Hz), 2.38, CH 3.90 (m), NH 8.38. – $^{13}$C NMR ($CDCl_3$): $(CH_3)_2$ δ = 21.1, $CH_3$ 23.3, $(CH_3)_3$ 28.4, CH 49.8, C 42.3, C-1 187.4, C-3 172.9, *ipso-*, *p*-C 134.7, 131.2, *o-*, *m*-C 129.3, 124.9.

$[C_{16}H_{25}N_2]SbCl_6$ (579.9) Calc. C 33.13 H 4.35 N 4.83 Found C 33.00 H 4.30 N 4.71

*1-tert-Butyl-3-isopropyl-3-(isopropylamino)-1-phenyl-2-azaallenium hexachloroantimonate* (**16b**): From **14b** (4.47 g) and **15b** (1.61 g). Yield 4.80 g (79%) of a colourless powder; m.p. 149 – 151 °C (dec.). – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.17 (d, $J$ = 7.0 Hz), 1.40, 1.44 (d, $J$ = 6.6 Hz), CH 2.94 (sept, $J$ = 6.6 Hz), 3.85 (m), NH 7.66. – $^{13}$C NMR ($CDCl_3$): $(CH_3)_2$ δ = 20.0, 21.1, $(CH_3)_3$ 28.7, CH 36.4, 49.3, C 42.5, C-1 185.2, C-3 177.1, *ipso-*, *p*-C 135.0, 131.4, *o-*, *m*-C 129.3, 125.1.

$[C_{18}H_{29}N_2]SbCl_6$ (607.9) Calc. C 35.56 H 4.81 N 4.61 Found C 35.47 H 4.71 N 4.62

*1,3-Di-tert-butyl-1-(isopropylamino)-3-phenyl-2-azaallenium hexachloroantimonate* (**16c**): From **14c** (4.61 g) and **15b** (1.61 g). Yield 4.48 g (72%) of a colourless powder; m.p. 157 – 162 °C (dec.). – $^1$H NMR ($CDCl_3$, 323 K): $CH_3$ δ = 1.26, 1.42, 1.45 (d, $J$ = 6.7 Hz), 1.46 (d, $J$ = 6.7 Hz), CH 3.80 (m), NH 7.15 (d, $J$ = 9.5 Hz). – $^{13}$C NMR ($CDCl_3$, 353 K): $(CH_3)_2$ δ = 20.9, 21.4, $(CH_3)_3$ 28.2, 28.9, CH 49.6, C 42.7, 39.8, C-1 176.8, C-3 182.9, *ipso-*, *p*-C 135.0, 131.7, *o-*, *m*-C 129.4, 125.4.

$[C_{19}H_{31}N_2]SbCl_6$ (621.9) Calc. C 36.69 H 5.02 N 4.51 Found C 36.50 H 5.07 N 4.50

*1-tert-Butyl-3-(isopropylamino)-1,3-diphenyl-2-azaallenium hexachloroantimonate* (**16d**): From **14d** (4.81 g)[38] and **15b** (1.61 g). Yield 5.33 g (83%) of a colourless powder; m.p. 118 – 121 °C. – $^1$H NMR ($CD_2Cl_2$, 223 K): $CH_3$ δ = 1.29 (d, $J$ = 6.4 Hz), 1.49 (d), 1.47, CH 3.91 (m), NH 8.02. – $^{13}$C NMR ($CD_2Cl_2$, 223 K): $CH_3$ δ = 21.1, 21.9, $(CH_3)_3$ 28.3, CH 50.1, C 42.6, C-1 189.7, C-3 171.0, *ipso-*, *p*-C 136.2, 135.2, 130.9, 128.7, *o-*, *m*-C 130.5, 129.0, 128.1, 124.8.

$[C_{21}H_{27}N_2]SbCl_6$ (641.9) Calc. C 39.39 H 4.24 N 4.37 Found C 39.01 H 4.01 N 4.38

*1-tert-Butyl-3-(tert-butylamino)-3-(diisopropylamino)-1-phenyl-2-azaallenium hexachloroantimonate* (**16e**): From **14e**[39] (5.18 g) and **15b** (1.61 g). Yield 6.38 g (93%) of a colourless powder; m.p. 170 – 172 °C (dec.). – $^1$H NMR ($CDCl_3$): $(CH_3)_2$ δ = 0.67 (broad), 1.19 (broad), $(CH_3)_3$ 1.19, 1.45, CH 3.67 (broad), 3.83 (broad), NH 5.28. – $^{13}$C NMR ($CDCl_3$): $(CH_3)_2$ δ = 20.4 (broad), $(CH_3)_3$ 29.1, 30.2, CH 50.4 (broad), C 42.9, 57.7, C-1 190.6, C-3 159.8, *ipso-*, *p*-C 134.4, 131.5, *o-*, *m*-C 129.3, 126.0.

$[C_{22}H_{38}N_3]SbCl_6$ (679.0) Calc. C 38.91 H 5.64 N 6.19 Found C 39.03 H 5.80 N 6.17

*1-tert-Butyl-3-(isopropylamino)-3-(isopropylmethylamino)-1-phenyl-2-azaallenium hexachloroantimonate* (**16f**): From **14f**[40] (4.76 g) and **15b** (1.61 g). Yield 4.59 g (72%) of a colourless

powder; m.p. 172–176°C (dec.). – $^1$H NMR ($CDCl_3$): $(CH_3)_2$ δ = 0.91 (broad), 1.09 (broad), 1.25 (broad), $(CH_3)_3$ 1.37, 1.38, $NCH_3$ 2.87, 2.96, CH 3.62 (m), 3.88 (m), 4.07 (m), NH 5.58 (d, *J* = 9 Hz), 5.82 (d, *J* = 9 Hz).

$[C_{19}H_{32}N_3]SbCl_6$ (637.0) Calc. C 35.83 H 5.06 N 6.60 Found C 35.86 H 5.04 N 6.51

*1-Isopropyl-1-(isopropylamino)-3,3-diphenyl-2-azaallenium hexachloroantimonate* (**16g**): From **14b** (4.47 g) and **15a**[41] (1.81 g). Yield 5.59 g (89%) of a colourless powder; m.p. 133–137°C. – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.22 (d, *J* = 7.0 Hz), 1.45 (d, *J* = 6.4 Hz), CH 3.10 (sept, *J* = 7.0 Hz), 3.99 (m), NH 8.06. – $^{13}$C NMR ($CDCl_3$): $CH_3$ δ = 20.4, 21.0, CH 36.7, 49.6, C-1 170.8, C-3 177.5, *ipso-*, *p*-C 134.2, 133.9, *o-*, *m*-C 130.2, 129.6.

$[C_{20}H_{25}N_2]SbCl_6$ (627.9) Calc. C 38.26 H 4.01 N 4.46 Found C 38.13 H 3.90 N 4.41

*1-tert-Butyl-1-(isopropylamino)-3,3-diphenyl-2-azaallenium hexachloroantimonate* (**16h**): From **14c** (4.61 g) and **15a** (1.81 g). Yield 5.07 g (79%) of a colourless powder; m.p. 145–146°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.30, 1.40 (d, *J* = 6.6 Hz), CH 3.91 (m), NH 7.24. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 21.2, 28.5, C 41.3, CH 50.1, C-1 169.2, C-3 177.9, *ipso-*, *p*-C 134.7, 134.1, *o-*, *m*-C 130.6, 130.0.

$[C_{21}H_{27}N_2]SbCl_6$ (641.9) Calc. C 39.29 H 4.24 N 4.37 Found C 39.32 H 4.05 N 4.28

*1-(Isopropylamino)-1,3,3-triphenyl-2-azaallenium hexachloroantimonate* (**16i**): From **14d** (4.81 g) and **15a** (1.81 g). Yield 5.59 g (76%) of a colourless powder; m.p. 79–81°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.41 (d, *J* = 6.5 Hz), CH 4.11 (m), NH 8.56, ether 1.14, 3.44. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 21.6, CH 50.6, C-1 176.1, C-3 170.8, ether 15.4, 65.9.

$[C_{23}H_{23}N_2]SbCl_6 \cdot (C_2H_5)_2O$ (736.0) Calc. C 44.06 H 4.52 N 3.81
Found C 43.77 H 4.21 N 3.75

*1-(tert-Butylamino)-1-(dimethylamino)-3,3-diphenyl-2-azaallenium hexachloroantimonate* (**16j**): From **14g**[39] (4.62 g) and **15a** (1.81 g). Yield 4.50 g (70%) of a pale yellow powder; m.p. 150–152°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.51, 2.65, 3.16, NH 5.53. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 30.0, 39.6 (broad), C 57.6, C-1 161.3, C-3 177.2, *ipso-*, *p*-C 135.2, 134.1, *o-*, *m*-C 130.3, 129.7,

$[C_{20}H_{26}N_3]SbCl_6$ (642.9) Calc. C 37.36 H 4.08 N 6.54 Found C 37.57 H 4.09 N 6.47

*1-(Diisopropylamino)-1-(isopropylamino)-3,3-diphenyl-2-azaallenium hexachloroantimonate* (**16k**): From **14h**[40] (5.04 g) and **15a** (1.81 g). Yield 6.17 g (90%) of a colourless powder; m.p. 197–198°C (dec.). – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.12 (broad), 1.21 (d, *J* = 6.7 Hz), 1.48 (broad), CH 3.62 (m), 4.00 (sept, *J* = 7.0 Hz; 2H), NH 5.15 (d, *J* = 8.5 Hz). – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 20.4 (broad), 22.8, CH 47.5 (broad), 48.5, C-1 159.4, C-3 177.1, *ipso-*, *p*-C 134.7, 134.1, *o-*, *m*-C 130.1, 129.6.

$[C_{23}H_{32}N_3]SbCl_6$ (685.0) Calc. C 40.33 H 4.71 N 6.14 Found C 40.30 H 4.82 N 6.12

*1-(tert-Butylamino)-1-(diisopropylamino)-3,3-diphenyl-2-azaallenium hexachloroantimonate* (**16l**): From **14e** (5.18 g) and **15a** (1.81 g). Yield 5.66 g (81%) of a colourless powder; m.p. 208–210°C (dec.). – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 0.73, 1.49 (broad), 1.51, CH 3.60 (broad), 3.84 (broad), NH 5.45. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 20.5 (broad), 30.1, CH 47.0 (broad), 57.8, C-1 159.4, C-3 176.3, *ipso-*, *p*-C 135.0, 134.2, *o-*, *m*-C 130.5, 129.7.

$[C_{24}H_{34}N_3]SbCl_6$ (699.0) Calc. C 41.24 H 4.90 N 6.01 Found C 41.36 H 4.97 N 6.01

*1,1-(2,2'-Biphenyldiyl)-3-(isopropylamino)-3-phenyl-2-azaallenium hexachloroantimonate* (**16m**): From **14d** (4.81 g) and **15d**[42] (1.79 g). Yield 6.01 g (91%) of an orange-yellow powder;

m.p. 199–200°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.52 (d, $J$ = 6.4 Hz), CH 4.18 (m), NH 8.65. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 22.1, CH 52.8, C-1, -3 168.1, 171.0.

$[C_{23}H_{21}N_2]SbCl_6$ (659.9) Calc. C 41.86 H 3.31 N 4.25 Found C 41.91 H 2.97 N 4.14

*1,1-(2,2'-Biphenyldiyl)-3-(tert-butylamino)-3-(diisopropylamino)-2-azaallenium hexachloroantimonate* (**16n**): From **14e** (5.18 g) and **15d** (1.79 g). Yield 6.34 g (91%) of an orange powder; m.p. 189–190°C. – $^1$H NMR ($CD_2Cl_2$): $(CH_3)_2$ δ = 1.19 (broad), 1.68 (broad), $(CH_3)_3$ 1.39, CH 3.95 (broad), 4.19 (broad), NH 5.63. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 20.7 (broad), 30.2, CH 48.2 (broad), C 57.7, C-1 171.4, C-3 160.5, fluorene-C 144.4, 136.6, 132.6, 129.9, 126.1, 122.1.

$[C_{24}H_{32}N_3]SbCl_6$ (697.0) Calc. C 41.35 H 4.63 N 6.03 Found C 41.51 H 4.55 N 5.97

*1,1,3-Tri-tert-butyl-3-(isopropylamino)-2-azaallenium hexachloroantimonate* (**16o**): From **14c** (4.61 g) and **15c**[43] (1.41 g). Yield 3.07 g (51%) of a colourless powder; m.p. 241–245°C (dec.). – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.38 (d, $J$ = 6.4 Hz), 1.40, CH 3.30 (m), NH 5.71 (d, $J$ = 9.8 Hz). – $^{13}$C NMR ($CD_2Cl_2$): $(CH_3)_2$ δ = 22.1, $(CH_3)_3$ 28.4, 2$(CH_3)_3$ 29.8, CH 47.6, C 38.7, 44.8, C-1 185.1, C-3 162.0.

$[C_{17}H_{35}N_2]SbCl_6$ (602.0) Calc. C 33.92 H 5.86 N 4.66 Found C 33.83 H 6.00 N 4.66

*1,1-Di-tert-butyl-3-(isopropylamino)-3-phenyl-2-azaallenium hexachloroantimonate* (**16p**): From **14d** (4.81 g) and **15c** (1.41 g). Yield 3.61 g (58%) of a colourless powder; m.p. 193–194°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.40, 1.51 (d, $J$ = 6.4 Hz), CH 3.60 (m), NH 6.98. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 21.9, 29.8, CH, C 48.8, 46.0, C-1 190.1, C-3 157.3, *ipso-*, *p*-C 135.3, 127.7, *o-*, *m*-C 130.8, 127.4.

$[C_{19}H_{31}N_2]SbCl_6$ (622.0) Calc. C 36.69 H 5.02 N 4.51 Found C 36.80 H 5.07 N 4.57

*1,1-Di-tert-butyl-3-(tert-butylamino)-3-(diisopropylamino)-2-azaallenium hexachloroantimonate* (**16q**): From **14e** (5.18 g) and **15c** (1.41 g). Yield 6.33 g (96%) of a colourless powder; m.p. 215–220°C (dec.). – $^1$H NMR ($CD_2Cl_2$): $(CH_3)_2$ δ = 1.29 (broad), 1.52 (broad), $(CH_3)_3$ 1.46, 2$(CH_3)_3$ 1.43, CH 3.47 (broad), 4.03 (broad), NH 5.00. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 20.5 (broad), 21.3 (broad), 30.0, CH 51.3 (broad), C 47.1, 56.6, C-1 194.8, C-3 156.6.

$[C_{20}H_{42}N_3]SbCl_6$ (659.0) Calc. C 36.45 H 6.42 N 6.38 Found C 35.62 H 6.67 N 6.19

*1-tert-Butyl-3,3-bis(dimethylamino)-1-(isopropylamino)-2-azaallenium hexachloroantimonate* (**16r**): From **14c** (4.61 g) and **15e** (Fluka) (1.15 g). After recrystallization from methanol (20 ml) yellow needles (4.38 g, 76%); m.p. 220–222°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.26 (d, $J$ = 7 Hz), 1.27, 3.00, CH 3.64 (m), NH 5.72. – $^{13}$C NMR ($CD_2Cl_2$): $(CH_3)_2$ δ = 22.9, $(CH_3)_3$ 28.4, $NCH_3$ 41.2, CH 45.6, C 39.9, C-1 168.2, C-3 163.6.

$[C_{13}H_{29}N_4]SbCl_6$ (575.9) Calc. C 27.11 H 5.08 N 9.73 Found C 27.18 H 5.30 N 9.70

*1,1-Bis(dimethylamino)-3-(isopropylamino)-3-phenyl-2-azaallenium hexachloroantimonate* (**16s**): From **14d** (4.81 g) and **15e** (1.15 g). Yield 4.35 g (73%) of a yellow powder; m.p. 180–181°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.40 (d, $J$ = 6.7 Hz), 2.84, CH 4.35 (m), NH 6.38. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 22.2, 41.2, CH 46.3, C-1, -3 167.4, 165.7, *ipso-*, *p*-C 133.5, 133.3, *o-*, *m*-C 130.3, 126.6.

$[C_{15}H_{25}N_4]SbCl_6$ (595.9) Calc. C 30.23 H 4.23 N 9.41 Found C 29.95 H 4.08 N 9.36

*1-(tert-Butylamino)-1-(diisopropylamino)-3,3-bis(dimethylamino)-2-azaallenium hexachloroantimonate* (**16t**): From **14e** (5.18 g) and **15e** (1.15 g). Yield 4.75 g (75%) of yellow prisms; m.p. 195–196°C. – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.36 (d, $J$ = 7.0 Hz), 1.43, 2.96, CH 3.78 (sept, $J$ = 7.0 Hz), NH 5.00. – $^{13}$C NMR ($CDCl_3$): $CH_3$ δ = 21.3, 30.0, 40.3, CH 48.0, C 55.0, C-1, -3 159.4, 156.3.

$[C_{16}H_{36}N_5]SbCl_6$ (633.0) Calc. C 30.36 H 5.73 N 11.07 Found C 30.47 H 5.88 N 11.04

*1-(tert-Butylamino)-1,3,3-tris(dimethylamino)-2-azaallenium hexachloroantimonate* (**16u**): From **14g** (4.62 g) and **15e** (1.15 g). Yield 3.92 g (68%) of yellow prisms; m.p. 208°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.44, 2.85 (6H), 2.90 (12H), NH 5.34. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 29.7, 38.7 (2C), 40.3 (4C), C-1, -3 162.5, 158.4.

$[C_{12}H_{28}N_5]SbCl_6$ (576.9) Calc. C 24.98 H 4.89 N 12.14 Found C 24.89 H 5.08 N 11.97

*1-(Diisopropylamino)-3,3-bis(dimethylamino)-1-(isopropylamino)-2-azaallenium hexachloroantimonate* (**16v**): From **14h** (5.04 g) and **15e** (1.15 g). Yield 5.88 g (95%) of a yellow powder; m.p. 210–211°C (dec.). – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.26 (d, $J$ = 6.7 Hz), 1.33 (d, $J$ = 6.7 Hz, broad), 2.92, CH 3.19 (m, 1H), 4.20 (broad, 2H), NH 4.71 (d, $J$ = 9.5 Hz). – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 21.1 (broad), 23.7, 40.3, CH 47.0, 48.2 (broad), C-1, -3 161.9, 157.4.

$[C_{15}H_{34}N_5]SbCl_6$ (619.0) Calc. C 29.11 H 5.54 N 11.32 Found C 29.07 H 5.60 N 11.16

*1-(Diisopropylamino)-3,3-bis(dimethylamino)-1-(methylamino)-2-azaallenium hexachloroantimonate* (**16w**): From **14i**[40] (4.76 g) and **15e** (1.15 g). After recrystallization from methanol (20 ml) at –20°C yellow prisms (4.73 g, 80%); m.p. 135–136°C. – $^1$H NMR ($CD_2Cl_2$): $CH_3$ δ = 1.31 (d, $J$ = 7.0 Hz), 2.70 (broad), 2.92, CH 4.16 (broad), NH 5.67. – $^{13}$C NMR ($CD_2Cl_2$): $CH_3$ δ = 20.9, 30.2, 40.2, CH 48.3, C-1, -3 162.2, 158.8.

$[C_{13}H_{30}N_5]SbCl_6$ (590.9) Calc. C 26.42 H 5.11 N 11.86 Found C 26.50 H 5.09 N 11.76

*1-tert-Butyl-3-(isopropylmethylamino)-1,3-diphenyl-2-azaallenium hexachloroantimonate* (**16x**): To **16d** (1.28 g, 2 mmol) in dichloromethane (10 ml) was added dropwise at –5°C an ethereal solution of diazomethane till the yellow colour persisted. Stirring was continued for 3 h at +22°C and then the solvent was evaporated. The residue was dissolved in dichloromethane (5 ml). After filtration with a little active charcoal and cooling to –50°C the product was precipitated by slow addition of ether (50 ml) affording a colourless powder (1.08 g, 82%); m.p. 177–180°C. – $^1$H NMR ($CDCl_3$): $NCH_3$ δ = 3.27, 3.43. – $^{13}$C NMR ($CDCl_3$): $(CH_3)_2$ δ = 18.7, 20.3, $(CH_3)_3$ 28.2, 28.3, $NCH_3$ 33.4, 35.6, CH 54.6, 56.5, C 42.1, 42.3, C-1 190.8, 190.0, C-3 172.8, 171.8.

$[C_{22}H_{29}N_2]SbCl_6$ (656.0) Calc. C 40.28 H 4.46 N 4.27 Found C 40.35 H 4.46 N 4.20

*X-ray diffraction analysis of* **16o**[*]

**16o**, $[C_{17}H_{35}N_2]^+$ $[SbCl_6]^-$, triclinic, space group $P\bar{1}$ (No. 2[44]), $Z$ = 2, $a$ = 1031.9 (3), $b$ = 1038.4 (3), $c$ = 1388.0 (7) pm, α = 103.85 (3)°, β = 110.37 (3)°, γ = 95.72 (3)°, $V$ = 1326 · $10^6$ pm$^3$, $d_r$ = 1.51 gcm$^{-3}$, $\mu_{Mo\text{-}K_\alpha}$ = 16.5 cm$^{-1}$, $T$ = 228 K, ω-scan, Δω = 1.0°, 1.5 < $\dot{\omega}$ < 29.3° min$^{-1}$, 2° < 2Θ < 42°, 2587 independent significant reflections ($I \geq 3\sigma$). The cell constants and reflections were measured from a crystal with dimensions 0.1 × 0.2 × 0.3 mm$^3$, sealed in a glass capillary, on a Syntex-P3-diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K_\alpha}$ = 71.069 pm. The structure was solved by direct methods using the program SHEL-XTL[45]. The *tert*-butyl groups were refined as rigid groups. Hydrogen atoms were fixed on calculated geometrically ideal positions. The partially anisotropic refinement led to agreement factors $R_1$ = 0.067 and $R_2$ = 0.072.

[*] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 50548, author, and the reference to this publication.

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