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The Structure of 2-Azaallenium Cations

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According to an *X*-ray structural analysis, the 2-azaallenium hexachloroantimonate **23** crystallizes with the topology of an allene (geometry **1a**) and not of a 2-azaallyl cation (**1b**). *Ab initio* molecular orbital calculations (3 – 21 G basis set) and semiempirical MNDO calculations for the unsubstituted 2-azaallenium cation and for some mono- and disubstituted derivatives (**24**) confirm the experimental results: In many cases the allenium geometry **24a** is more stable than the 2-azaallylium form **24b**. Electron-releasing substituents reduce the energy difference between **24b** and **24a**. With two amino substituents the allylium geometry **24b** is energetically preferred to the allenium form **24a**. In general, substituted 2-azaallenium salts are sterically flexible around the central nitrogen atom. Compound **23** was synthesized by a new method.

Zum Bau von 2-Azaallenium-Kationen

Entsprechend einer Röntgenstrukturanalyse kristallisiert das 2-Azaallenium-hexachloroantimonat **23** in der Topologie eines Allens (Geometrie **1a**) und nicht eines 2-Azaallyl-Kations (**1b**). Ab-initio-Molekülorbital- (3 – 21 G Basissatz) und semiempirische MNDO-Rechnungen für das unsubstituierte 2-Azaallenium-Kation und einige mono- und disubstituierte Derivate (**24**) bestätigen die experimentellen Befunde: In vielen Fällen ist die Allengeometrie **24a** stabiler als die 2-Azaallylium-Form **24b**. Elektronenspendende Substituenten verringern den Energieunterschied zwischen **24b** und **24a**. Ein diaminosubstituiertes Allylium-Kation **24b** ist energetisch stabiler als die entsprechende Allenium-Form **24a**. Ganz allgemein sind substituierte 2-Azaallenium-Kationen um das zentrale Stickstoffatom sterisch flexibel. Verbindung **23** wurde nach einer neuen Synthese hergestellt.

Forty-five classes of formal 2-azaallenium compounds can be constructed from the elements of the first period of eight if the number of unit charges is restricted to one per atom and the number of electron pairs of the allene unit to eight. Of these, seventeen classes contain carbon and therefore may be classified as organic (Table 1).

According to qualitative valence bond (VB) arguments for many of these molecules two (e. g. **a** and **b**) or more valence tautomeric forms can be drawn. It is not always easy to predict whether in the ground states these compounds are allenes (**a**) with linear $\rangle C = \overset{+}{N} = X \langle$ moieties and planes through $\rangle C =$ and $= X \langle$, which are perpendicular with respect to one another, or pseudoallenes[11] with other topologies (e. g. **b**). For instance, nitrile oxides, **15**, are known[10] to be linear pseudoallenes (**b**), whereas *ab initio* calculations predict[2] for the related nitrile ylides, **2**, to resemble geometrically allenyl anions (**a**). In this paper structural features of 2-azaallenium salts **1**[1,12–14] are reported.

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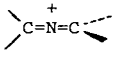
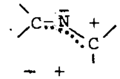
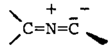
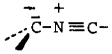
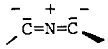
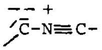
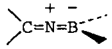
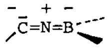
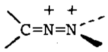
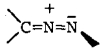
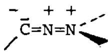
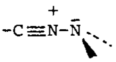
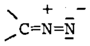
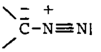
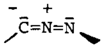
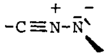
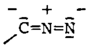
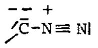
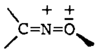
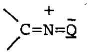
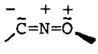
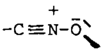
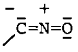
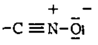
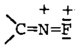
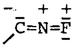
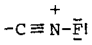
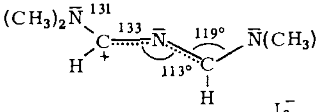
Table 1. Formal Organic 2-Azaallenium Compounds Containing only Atoms of the Second Period and not more than One Electric Charge Unit per Atom and a Total of Eight Pairs of Electrons

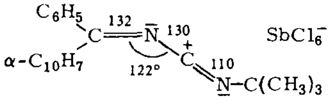
Compound	Geometry a		b	Name references)
1		⇌		2-azaallenium ions 1)
2		⇌		nitrile ylides 2)
3		⇌		
4				(methyleneamino)boranes 3,4)
5				
6				
7				azocarbenium ions
8		⇌		nitrile amines 5)
9		⟷		diazoalkanes 6)
10				nitrile imines 2)
11		⟷		deprotonated diazoalkanes 7–9)
12				
13				
14		⇌		nitrile alkoxides 5)
15		⇌		nitrile oxides 10)
16				
17		⇌		nitrile fluorides

For the double Mannich salts **1** the allene geometry **a** with local D_{2d} symmetry and a planar 2-azaallyl topology **b** (local C_{2v} symmetry) with bent CNC unit will be considered. In form **a** two π bonds are orthogonal with respect to one another while in form **b** the lone pair of the nitrogen atom is perpendicular to the π system of an allyl cation. Molecular structures have been determined for some heterosubstituted salts **1**[15–21].

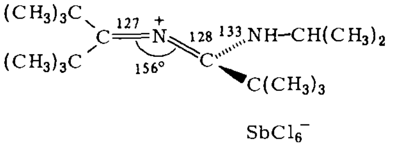
According to X-ray diffraction data, Gold's reagent, **18** (triiodide[15]), and the formal 1,3-diazabutatrienium compound **19**[16] have the structural features of form **1b**. On the other hand, the amino-substituted 2-azaallenium compound **20** closely resembles **1a**[17]. The planes through the molecular halves are perpendicular (angle β) with respect to one another. The central CNC moiety shows little bending and the C = N bonds are short. The phenylogue of a tetraamino-substituted 2-azaallenium ion **21**[18] and several monoprotonated biguanides **22**[19–21] crystallize in geometries intermediate to those of forms **1a** and **1b**. The CNC units are bent in both molecules. These data suggest that heterosubstituted 2-azaallenium ions **1** might sterically be rather flexible.



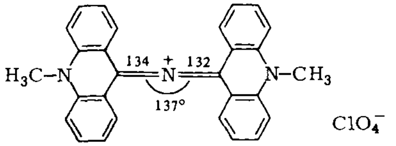
18



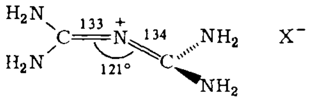
19



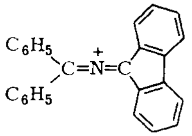
20, ß ≈ 90°



21, ß ≈ 66°



22, ß = 40-50°



23

Since structures of 2-azaallenium salts without hetero substituents have not been reported, an X-ray structure analysis for the 2-azaallenium hexachloroantimonate **23** was carried out. Furthermore, semiempirical and *ab initio* molecular orbital calculations for several 2-azaallenium cations are reported.

X-Ray Diffraction Analysis for 23[*]

23, $[C_{26}H_{18}N]^+[SbCl_6]^-$, monoclinic, space group $P2_1/c$ (No. 14[22]), $Z = 4$, $a = 1161(1)$, $b = 1060.5(4)$, $c = 2579(3)$ pm, $\beta = 121.93(6)°$, $V = 2695 \cdot 10^6$ pm^3, $d_{\text{calc.}} = 1.67$ gcm^{-3}, $\mu_{\text{Mo-}K_\alpha} = 16.4$ cm^{-1}, $T = 240$ K, ω-scan, $\Delta\omega = 1.1°$, $1.8 < \dot{\omega} < 29.3°$ min^{-1}, $2° < 2\Theta < 42°$, 2618 independent significant reflections ($I > 2\sigma$). The cell constants and the intensities were determined on a Syntex P 3 diffractometer (graphite monochromator, $\lambda_{\text{Mo-}K_\alpha} = 71.069$ pm). The structure was solved by direct methods using the program SHEL-XTL[23]. Hydrogen atoms were

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[*] 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 the registry number CSD 50678, authors, and source.

Table 2. Fractional Atomic Coordinates and Thermal Parameters for **23**[a)]

Atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Sb	0.09996(6)	0.35486(5)	0.39442(3)	0.0376(4)	0.0280(3)	0.0409(4)	0.0018(3)	0.0204(3)	-0.0054(3)
Cl1	0.0661(3)	0.4742(2)	0.3100(1)	0.056(2)	0.055(2)	0.051(2)	0.015(1)	0.027(1)	-0.009(1)
Cl2	0.1327(3)	0.2361(2)	0.4786(1)	0.063(2)	0.048(2)	0.053(2)	0.015(1)	0.030(1)	-0.005(1)
Cl3	0.3193(3)	0.4399(3)	0.4551(1)	0.053(2)	0.092(2)	0.053(2)	0.006(2)	0.017(1)	-0.035(2)
Cl4	-0.1189(3)	0.2689(3)	0.3330(1)	0.049(2)	0.070(2)	0.060(2)	0.009(1)	0.015(1)	-0.024(1)
Cl5	0.0096(3)	0.5205(3)	0.4231(2)	0.111(2)	0.043(2)	0.104(2)	0.001(2)	0.077(2)	0.011(2)
Cl6	0.1906(3)	0.1869(3)	0.3667(1)	0.104(2)	0.056(2)	0.092(2)	0.000(2)	0.069(2)	0.018(2)
N	0.3836(7)	0.1289(7)	0.2761(3)	0.042(5)	0.051(5)	0.053(5)	0.002(4)	0.023(4)	0.010(4)
C1	0.4450(8)	0.0853(8)	0.3299(4)	0.040(5)	0.037(5)	0.043(5)	0.001(4)	0.024(5)	0.012(4)
C2	0.3553(8)	0.1647(8)	0.2231(4)	0.035(5)	0.036(5)	0.037(5)	-0.003(4)	0.015(4)	-0.007(4)
C3	0.4060(9)	-0.0244(8)	0.3525(4)	0.037(5)	0.033(5)	0.049(6)	-0.011(5)	0.020(5)	0.005(4)
C4	0.2977(9)	-0.1058(9)	0.3203(5)	0.047(6)	0.037(6)	0.068(7)	-0.016(5)	0.024(5)	0.006(5)
C5	0.289(1)	-0.205(1)	0.3536(6)	0.049(7)	0.040(6)	0.10(1)	-0.019(6)	0.034(7)	-0.003(5)
C6	0.383(1)	-0.2193(9)	0.4144(6)	0.073(8)	0.028(6)	0.12(1)	0.001(7)	0.060(8)	-0.001(6)
C7	0.493(1)	-0.1356(9)	0.4470(5)	0.058(7)	0.035(6)	0.071(7)	0.011(6)	0.036(6)	0.007(5)
C8	0.5021(9)	-0.0382(8)	0.4138(4)	0.045(6)	0.037(6)	0.051(6)	0.000(5)	0.028(5)	0.009(5)
C9	0.6038(8)	0.0648(8)	0.4336(4)	0.041(5)	0.029(5)	0.045(5)	0.000(4)	0.025(5)	0.004(4)
C10	0.7173(9)	0.0918(9)	0.4881(4)	0.048(6)	0.043(6)	0.044(6)	0.003(5)	0.014(5)	0.002(5)
C11	0.797(1)	0.196(1)	0.4913(5)	0.044(6)	0.049(6)	0.058(7)	-0.005(5)	0.009(5)	0.007(5)
C12	0.765(1)	0.2661(9)	0.4412(5)	0.051(6)	0.041(6)	0.074(7)	0.003(5)	0.031(6)	-0.008(5)
C13	0.6487(9)	0.2387(9)	0.3860(4)	0.051(6)	0.038(6)	0.061(6)	0.015(5)	0.036(5)	0.001(5)
C14	0.5686(9)	0.1391(8)	0.3822(4)	0.045(6)	0.034(5)	0.045(6)	0.002(5)	0.026(5)	0.009(5)
C15	0.2484(8)	0.2579(8)	0.1891(4)	0.025(5)	0.031(5)	0.037(5)	-0.010(4)	0.007(4)	0.000(4)
C16	0.1451(9)	0.2730(9)	0.2014(4)	0.041(6)	0.038(6)	0.056(6)	-0.009(5)	0.019(5)	-0.002(5)
C17	0.0486(9)	0.366(1)	0.1700(5)	0.033(5)	0.058(7)	0.074(7)	-0.021(6)	0.020(5)	0.000(5)
C18	0.058(1)	0.4415(9)	0.1287(5)	0.045(6)	0.042(6)	0.058(7)	-0.010(5)	0.005(5)	0.005(5)
C19	0.159(1)	0.4291(9)	0.1180(5)	0.059(7)	0.035(6)	0.065(7)	0.004(5)	0.024(6)	-0.001(5)
C20	0.2544(9)	0.3365(8)	0.1476(4)	0.056(6)	0.028(5)	0.051(6)	-0.004(5)	0.030(5)	0.001(5)
C21	0.4311(9)	0.1083(7)	0.1981(4)	0.044(5)	0.022(5)	0.048(5)	0.005(4)	0.026(5)	0.004(4)
C22	0.5681(9)	0.0795(9)	0.2378(4)	0.045(6)	0.046(6)	0.049(6)	0.016(5)	0.023(5)	0.011(5)
C23	0.642(1)	0.028(1)	0.2152(5)	0.070(7)	0.049(6)	0.069(7)	0.013(6)	0.046(6)	0.016(6)
C24	0.580(1)	0.0020(9)	0.1555(5)	0.066(7)	0.044(6)	0.093(8)	0.011(6)	0.058(7)	0.013(5)
C25	0.446(1)	0.0289(9)	0.1158(4)	0.092(8)	0.040(6)	0.053(6)	0.000(5)	0.050(6)	0.000(6)
C26	0.3692(9)	0.0830(8)	0.1372(4)	0.056(6)	0.035(5)	0.051(6)	0.004(5)	0.034(5)	0.001(5)

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

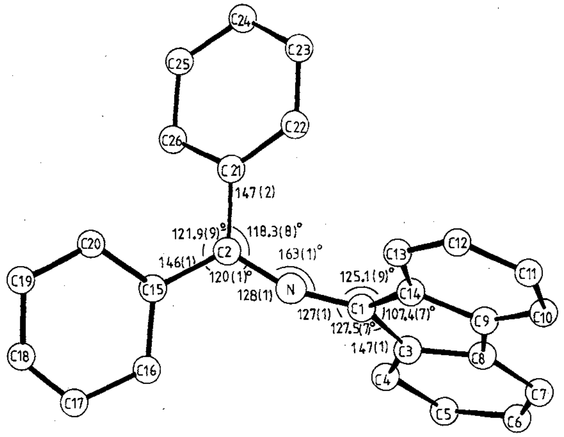


Fig. 1. Molecular Plot with Selected Bond Lenghts [pm] and Bond Angles [°] for the Cation of **23**[a)]

[a)] Torsional angles: C15 – C2 – N – C1 – 157(3), C2 – N – C1 – C3 – 119(3), C21 – C2 – N – C1 + 24(3), C2 – N – C1 – C14 + 63(3), N – C2 – C21 – C22 – 36(1), N – C2 – C15 – C16 – 24(1), C16 – C15 – C2 – C21 + 155.0(8), C15 – C2 – C21 – C22 + 145.1(8), N – C1 – C14 – C13 – 4(2), N – C1 – C3 – C4 + 2(2), C3 – C1 – C14 – C13 + 178(1), angle between the planes through C15-C21-N and C3-C4-N – 95°.

fixed on calculated geometrically ideal positions. Atomic factors of neutral atoms were used. Anisotropic full-matrix least square refinement led to agreement factors $R_1 = 0.047$ and $R_2 = 0.053$.

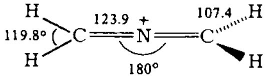
A list of atomic coordinates with LS-computed standard deviations is given in Table 2. Fig. 1 shows a molecular plot with selected bond lengths and bond angles for the cation of **23**.

The crystals of **23** consist of discrete $[C_{26}H_{18}N]^+$ cations and $SbCl_6^-$ anions. The angle β between the planes through C15-C21-N and C3-C4-N amounts to 85°. The C1 – N – C2 unit shows slight bending (163°). The bonds C1 – N (127 pm) and C2 – N (128 pm) are shorter than those in **21** (132, 134 pm), but are comparable to the corresponding bonds in **20**. Therefore, both compounds **20** and **23** should be regarded as allenes (**1a**) and not as 2-azaallylium cations (**1b**). The similarity of the geometries of **20** and **23** suggests that the electronic influence of the amino substituents on the structure of **20** is small. According to the *X*-ray data for **18** – **23** the geometry of the salts **1** seems to be mainly determined by the steric demands of the substituents, in agreement with the assumption that the salts **1** are flexible around the nitrogen atom.

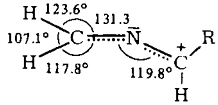
Quantum Mechanical Calculations

Methods: The 3 – 21 G basis set of the Gaussian 76 series of programs[24,25] and the semiempirical MNDO method[26] were employed to calculate the energies of completely optimized geometries of several 2-azaallenium cations **24**.

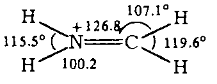
Results: The 3 – 21 G calculations for $H_2C\overset{+}{N}CH_2$ resulted in a linear structure **24a** (R^i = H) with D_{2d} symmetry (total energy E(RHF) = – 132.01960 a. u.; $E_{rel.}$ = 0.0 kJmol^{-1}).



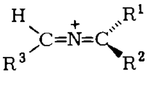
24a (R^i = H), D_{2d}



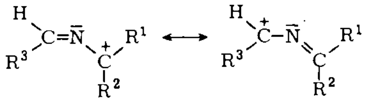
24b (R^i = H), C_{2v}



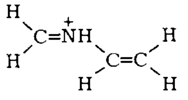
25, C_{2v}



24a



24b



26

The calculated C = N bond length (123.9 pm) is markedly shorter than that of **25** (3 – 21 G: 126.8 pm, experimental: 127.2 pm[27]). A similar shortening of the C = C double bond is observed for allene (129.4 pm) in comparison with ethene (132.0 pm) (3 – 21 G). This can be explained by the change in hybridization from sp^2 to sp and concomitant enhancement of the electronic charge density around the nucleus of the central N or C atom, respectively. The C – H distances and the N – C – H bond angles in **24a** (R^i = H) and **25** are similar, thus justifying the denotation of **24a** as double Mannich ion.

Geometry optimization of the 2-azaallyl cation **24b** (R^i = H) led without an activation barrier to structure **24a** (R^i = H). If **24** is forced to remain planar during the optimization the structure **24b** results, which must therefore be regarded as the lowest energy transition state ($E_{rel.}$ = 174.9 kJmol^{-1}) of the hindered rotation of a CH_2 group around the H_2C-N bond in **24a** (R^i = H)[28]. Being a saddle point on the potential energy surface a molecule **24b** (R^i = H) should be experimentally inaccessible.

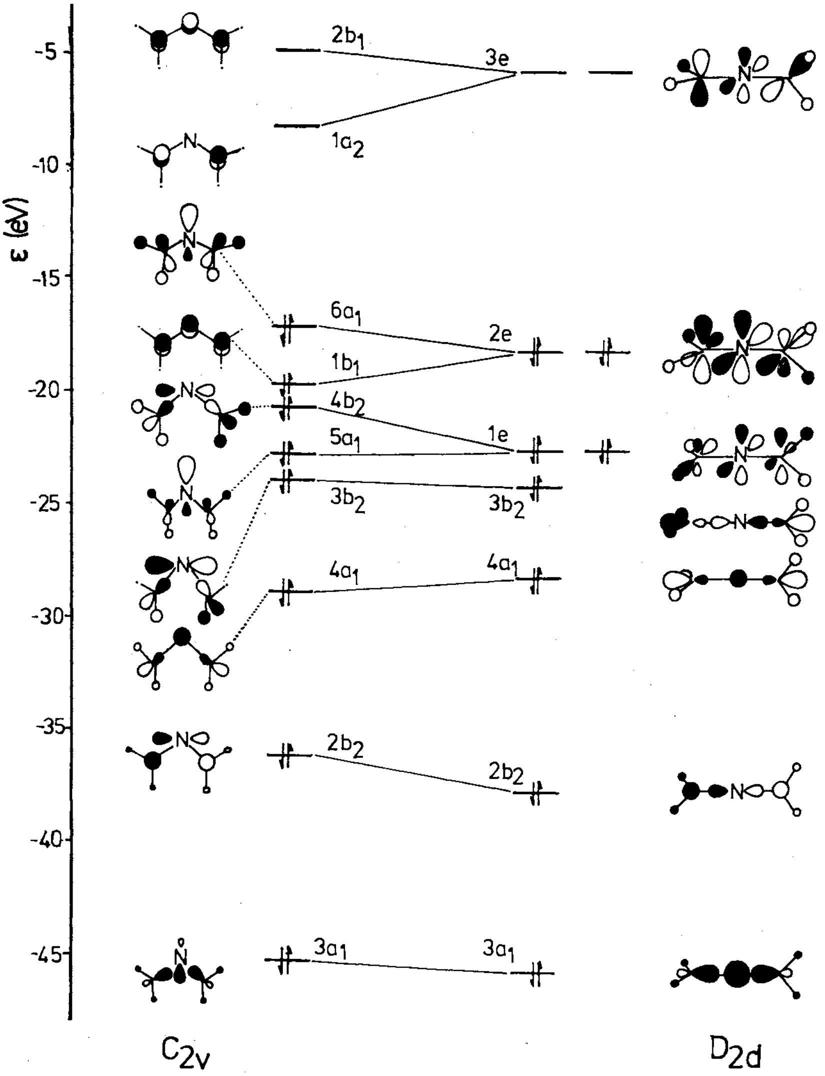


Fig. 2. MO Correlations of the C_{2v} Geometry of **24b** (R^i = H) and the D_{2d} Geometry of **24a** (R^i = H) (MNDO data)

The electronic reason for the observed preference of the linear allenium structure **24a** (R^i = H) over the valence tautomeric 2-azaallylium form **24b** (R^i = H) can be seen from Fig. 2, which shows an orbital correlation diagram for the interconversion of the two isomers (MNDO data). Going from the bent C_{2v} structure (**24b**, R^i = H) to the linear D_{2d} symmetry (**24a**, R^i = H) the energy changes of many orbitals compensate each other (e.g. $6a_1 \rightarrow 2e$ and $1b_1 \rightarrow 2e$). But for two orbitals ($4b_2$, $2b_2$) the transformation is associated with a significant energy gain. In both cases the in-phase overlaps of the nitrogen p_x orbital are increased on going to the linear form (D_{2d}).

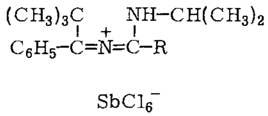
In spite of the large energy difference between **24a** (R^i = H) and **24b** (R^i = H) the 2-azaallenium cation should be rather flexible. Contracting the C – N – C angle from 180 to 120° raises the energy of **24a** (R^i = H) by more than 170 $kJmol^{-1}$, but bending to 160° requires only 16 $kJmol^{-1}$. This bending energy is further reduced by electron donating substituents. Therefore, deviations from geometry **1a** as found for **23** could well result from packing forces in the crystal.

In Table 3 calculated energy differences of some monosubstituted 2-azaallyl cations **24b** (restricted to C_s symmetry, full-geometry optimization) and the more stable 2-azaallenium ions **24a** are given. These relative energies strongly depend on the electron releasing properties of the substituents. The energy difference (3 – 21 G: 174.9 $kJmol^{-1}$) of the valence tautomers **24b** and **a** (R^i = H) is reduced to 146.7 $kJmol^{-1}$ by introduction of a methyl substituent. Such compounds are experimentally inaccessible because they tautomerize to **26**[29].

Table 3. Energy Differences Between Substituted 2-Azaallyl (**24b**) and 2-Azaallenium Cations (**24a**)

R^1	R^2	R^3	E(**24b**) – E(**24a**) [$kJmol^{-1}$] 3 – 21 G	MNDO
H	H	H	174.9	98.3
Cl	H	H	149.4	85.4
CH_3	H	H	146.7	86.5
F	H	H	132.2	64.0
OH	H	H	95.8	52.3
H	OH	H	82.2	35.9
C_6H_5	H	H	–	38.1
NH_2	H	H	29.6	8.8
NH_2	NH_2	H	– 8.5	– 15.9
NH_2	H	NH_2	– 17.5	– 18.8

Chlorine and methyl exert similar substituent effects. Due to a better compensation of bond dipole moments, a transition state **24b** with an *cis*-OH group is more stable than that with the hydroxyl substituent in *trans*-position. Because of combined bond angle closing and simultaneous rotation of the methylene groups passing through a transition state **24b** oxy substituted 2-azaallenium salts (**24a**, R^2 = OR, $R^{1,3}$ = H[30,31]) are predicted to be sterically instable at room temperature. The most efficient substituent is the amino group, which lowers the barrier between **24b** and **24a** (R^1 = NH_2, $R^{2,3}$ = H) to 29.6 $kJmol^{-1}$. Therefore, such compounds are predicted to be very flexible. Experimentally, the following barriers to racemization have been found by dynamic ^{13}C NMR measurements[17]:



$$C_6H_5-\overset{(CH_3)_3C}{C}=\overset{+}{N}=\overset{NH-CH(CH_3)_2}{C}-R \qquad SbCl_6^-$$

R	$\Delta G^{\ddagger}$ [kJ mol^{-1}]
CH_3	36
$CH(CH_3)_2$	50
C_6H_5	52
$C(CH_3)_3$	>90

Introduction of a second amino group even reverses the stabilities: according to the 3−21 G calculations the allenes **24a** ($R^{1,3}$ or $R^{1,2}$ = NH_2) are now less stable than the planar 2-azaallyl cations **b** by 17.5 and 8.5 kJmol^{-1}, respectively. The *X*-ray results on Gold's reagent, **18**, are in agreement with these calculations.

The MNDO calculated substituent effects show the same trend as the 3−21 G results. Because of the large number of atoms only the MNDO has been employed to calculate the effect of a phenyl group (**24**, R^1 = C_6H_5, $R^{2,3}$ = H) on the equilibrium **24a** ⇌ **24b**. According to these calculations, a phenyl substituent increases the flexibility of a 2-azaallenium salt even more than a hydroxyl group (Table 3). A second phenyl substituent should further reduce this energy difference, although to a lesser extent than the first group because of sterically induced nonplanarity. In the optimized geometry **24a** (R^1 = C_6H_5, $R^{2,3}$ = H) the CH_2 group is turned away from the phenyl substituent ($\sphericalangle$ C−N−C = 177.05°). Fixing the C−N−C angle to 163°, the value measured for **23**, and optimizing all other geometrical parameters resulted in an increase of the energy by only 9.5 kJmol^{-1}. The planes of the methylene groups remain perpendicular with respect to one another. Again, small forces resulting from crystal packing or from the influence of the counter ion could be sufficient to explain the observes C−N−C bond angle in **23**. It may be noted that bending of the C−N−C moiety in **24a** (R^1 = C_6H_5, $R^{2,3}$ = H) to 163° has little influence on the calculated C=N bond length ($C_6H_5C=N_{lin.}$ = 129.9 pm, $H_2C=N_{lin.}$ = 127.3 pm; $C_6H_5C=N_{bent}$ = 129.9 pm, $H_2C=N_{bent}$ = 127.9 pm). Consequently, the influence of the C−N−C bending on the antisymmetric stretching vibration (**23**: 1880 cm^{-1}; CH_2Cl_2) should be small.

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Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer, dichloromethane solutions. – ^1H and ^{13}C NMR spectra: Bruker WM-250 spectrometer, δ-scale, external reference tetramethylsilane. – Melting points: uncorrected.

9-Chloro-9-isocyanatofluorene: To phosgene (19.78 g, 200 mmol) in anhydrous toluene (50 ml) was added dropwise at −5°C with stirring a solution of 9-fluorenimine[32] (13.44 g, 75 mmol) in anhydrous toluene (250 ml). Under vigorous stirring a stream of dry phosgene was passed through the reaction mixture, which was slowly heated to 120°C bath temperature[33]. When the solution became clear the solvent was evaporated under reduced pressure. The residue was recrystallized from anhydrous dichloromethane/pentane affording orange needles (17.22 g, 95%); m.p. 112−114°C. – IR: NCO 2250, CO[33] 1710 cm^{-1}.

$C_{14}H_8ClNO$ (241.7) Calcd. C 69.58 H 3.34 N 5.80 Found C 69.42 H 3.23 N 5.82

1,1-(2,2'-Biphenylylene)-3,3-diphenyl-2-azaallenium Hexachloroantimonate (**23**): To a stirred solution of 9-chloro-9-isocyanatofluorene (1.21 g, 5.00 mmol) and benzophenone (0.92 g, 5.05 mmol) in anhydrous dichloromethane (20 ml) was added dropwise at $-78\,^{\circ}C$ a solution of antimony pentachloride (1.50 g, 5.00 mmol, freshly distilled) in anhydrous dichloromethane (10 ml). The reaction mixture was warmed to 23 °C over a period of 6 h. Stirring was continued at that temperature for an additional 5 h. To the dark orange solution anhydrous pentane (50 ml) was slowly added affording a precipitate (2.89 g, 85%), which was recrystallized from hot acetonitrile giving red prisms; m. p. 218 – 225 °C. – ^{13}C NMR (CD_2Cl_2, 263 K): C-1 δ = 149.5, C-3 161.6, aromatic C 143.6, 138.2, 136.6, 131.9, 130.1, 130.0, 128.5, 127.2, 126.2, 122.9. – IR: $C=\overset{+}{N}=C$ 1880 (shoulder 1820), 1590 cm^{-1}.

$[C_{26}H_{18}N]SbCl_6$ (678.9) Calcd. C 46.00 H 2.67 N 2.06 Found C 45.90 H 2.77 N 2.07

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