1-Aza-2-azoniaallene salts: reactions with azomethines and other N-nucleophiles

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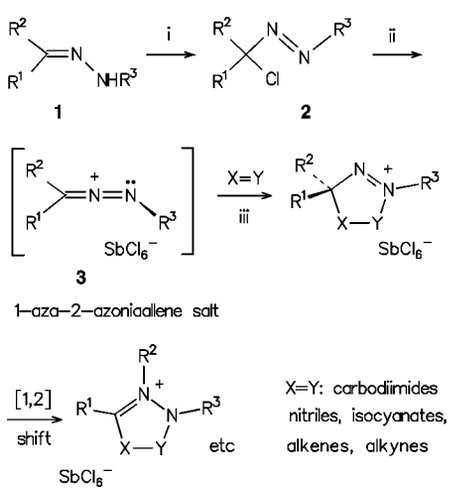
Azomethines undergo nucleophilic addition to 1-aza-2-azoniaallene salts **7** to furnish *N*-(azoalkyl)iminium salts (*e.g.* **10**, **12**, **13**). With cyclic hydrazones such as pyrazole or indazole, heterocumulenes **7** afford bicyclic 1,2,4,5-tetrazinium salts (*e.g.* **14**, **16**), or simple N-adducts such as **15**, **17**. On the other hand, with open-chain hydrazones azinium salts **19** are formed. Benzotriazole and the aziridine **21** react with 1-aza-2-azoniaallene salts **7** to afford (azoalkyl)ammonium salts **20**, **22**. The heterocumulenes **7** undergo cycloaddition across the C=N double bond of the azirine **23** to furnish azirenotriazolium salts **25**, while with the 1-aza-2-azoniaallene salt **3a** the triazolium salt **28** was formed. The constitutions of compounds **22**, **25a** and **28** were confirmed by X-ray structural analyses.

Introduction

1-Aza-2-azoniaallene salts **3** representing a new class of reactive intermediates disclosed by us a few years ago are prepared from hydrazones **1** by chlorination with *tert*-butyl hypochlorite and treatment of the resulting (1-chloroalkyl)azo compounds **2** with a Lewis acid, *e.g.* antimony pentachloride (Scheme 1).[1] The

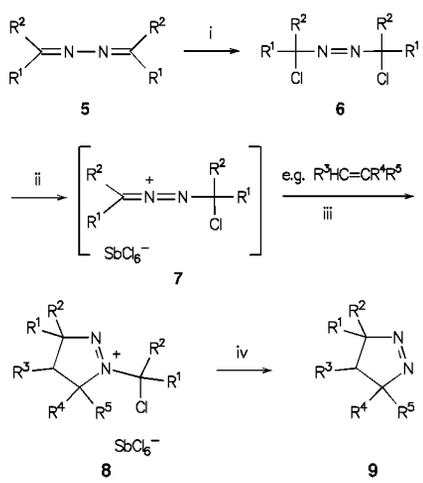


Scheme 1 *Reagents and conditions*: i, Me_3COCl, $CHCl_3$, 0 °C, 3 h, exclusion of light; ii, $SbCl_5$, CH_2Cl_2, −60 °C; iii, CH_2Cl_2, −60 °C to 23 °C, 130 min.

heterocumulene salts **3** behave as cationic four-electron components undergoing cycloaddition to all types of multiple bonds studied so far. Thus, heterocycles **4** were obtained by cycloaddition of compounds **3** to nitriles,[1,2] carbodiimides,[3] isocyanates,[4] alkenes,[2,5–7] alkynes[5,6] and isothiocyanates.[8,9]

The reactive 1-(1-chloroalkyl)-1-aza-2-azoniaallene salts **7** proved to be especially useful for cycloadditions because the primary products, *e.g.* **8**, are easily hydrolyzed to electrically neutral heterocycles (*e.g.* **9**) (Scheme 2).[7] Azo compounds **6** are prepared from azines **5** by chlorination at low temperatures.[7,10–19] Treatment with one equivalent of a Lewis acid transforms the chloroazo compound **6** into the reactive intermediate **7**.[7]

Arguments in favour of a concerted reaction mechanism have been put forward for cycloadditions of **3** and **7** with alkynes



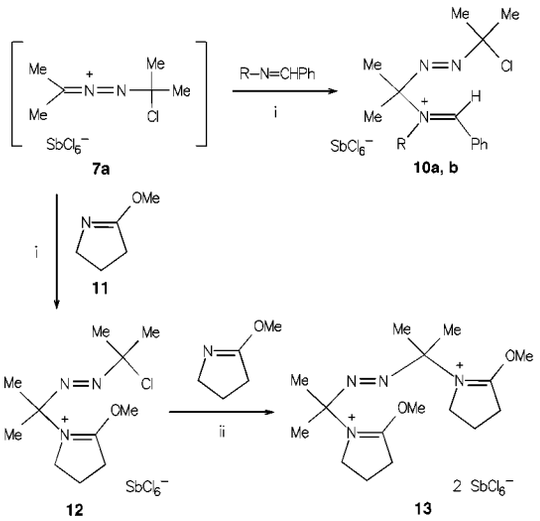
Scheme 2 *Reagents and conditions*: i, Cl_2, petroleum ether, −60 °C, 3 h; ii, $SbCl_5$, CH_2Cl_2, −60 °C; iii, −60 °C to 23 °C, 130 min; iv, $NaHCO_3$–NH_3–MeCN–H_2O, 0 °C, 2 h.

and alkenes (1,3-dipolar cycloaddition with inverse electron demand). On the other hand, reactions with carbodiimides, nitriles and isocyanates start with nucleophilic attack of a nitrogen atom on the C=N^+=N carbon atom giving respectively a nitrilium or an acylium salt intermediate, which cyclizes to the heterocycle.[1–7]

Since cumulated imines like carbodiimides and isocyanates react with 1-aza-2-azoniaallene salts **3** under mild conditions to give good yields of heterocycles **4**, it seemed worthwhile to extend these studies to reactions of heteroallenes **3**, **7** with azomethines with isolated C=N double bonds. The following report addresses this issue.

Results and discussion

When benzylidenemethylamine was treated between −60 °C and +23 °C with the heteroallene **7a** the rather moisture and temperature sensitive iminium salt **10a** was isolated in 58% yield (Scheme 3). Although a correct elemental analysis could not be obtained, the structure of **10a** was apparent from the NMR spectra which showed two pairs of equivalent *C*-methyl groups, an *N*-methyl group, a monosubstituted phenyl group, two ^{13}C signals for C–N and a ^{13}C resonance for the iminium carbon



Scheme 3 *Reagents and conditions*: i, CH_2Cl_2, −70 °C to −50 °C, 30 min, **10a**, R = Me, 58%, **10b**, R = Pr^i, 89%, **12**, 88%; ii, $SbCl_5$, CH_2Cl_2, −70 °C to −50 °C, 30 min, 83%.

atom at 172.7 ppm (in CD_3CN). Correspondingly, the salt **10b** was obtained (89%). However, the products of the reaction of the heteroallene **3a** (**3**, R^1, R^2 = Me, R^3 = 2,4,6-$Cl_3C_6H_2$) with benzylidenemethylamine or benzylideneisopropylamine decomposed on attempted isolation.

Reaction of the heteroallene **7a** with the electron-rich azomethine **11** afforded the stable adduct **12** (88%). With two equivalents of the isoamide **11** and two equivalents of antimony pentachloride the sensitive dication **13** was isolated (83%). The constitution of this salt was deduced from the symmetry of the NMR spectra and an (almost) correct elemental analysis.

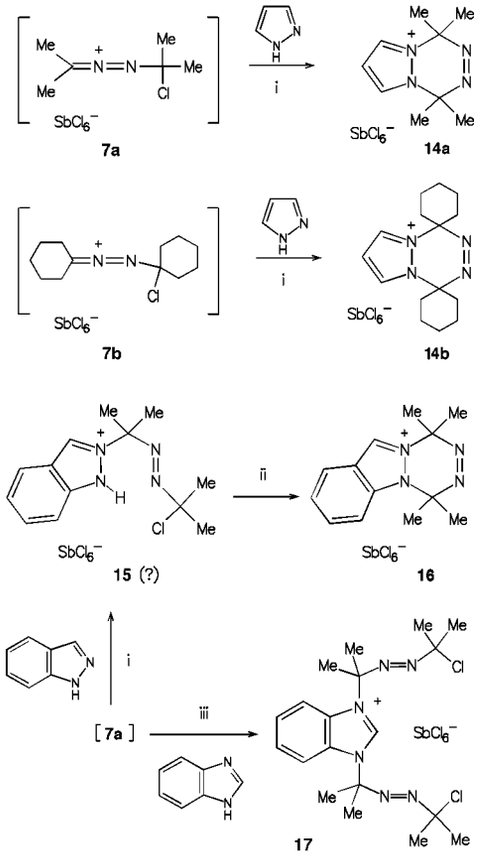
Thus, in contrast to cumulated imines (carbodiimides, isocyanates), which give cycloadducts with heterocumulenes **3**, simple azomethines undergo nucleophilic addition to the electron-deficient cumulated carbon atoms of **3**, **7**. This observation was further substantiated by reaction of **7a**,**b** with pyrazole (Scheme 4). Instead of cycloaddition across the C=N double bond, cycloaddition across N–NH took place affording the bicyclic tetrazinium salt **14a** (70%), apparently a new ring system. Similarly, with compound **7b** the salt **14b** was isolated (88%). With indazole and **7a** a labile monosubstituted product **15** was obtained (69%), the constitution of which is not yet clear. The product may be either a 1- or a 2-substituted indazolium salt. Heating compound **15** in dichloromethane resulted in ring closure furnishing the tricyclic salt **16** (57%) with unambiguous structure. Benzimidazole reacted with two equivalents of **7a** to afford the 1,3-disubstituted salt **17** (74%).

Recently, Uneyama and Sugimoto described an intramolecular addition of an 1-aza-2-azoniaallene cation to a C=N double bond.[20]

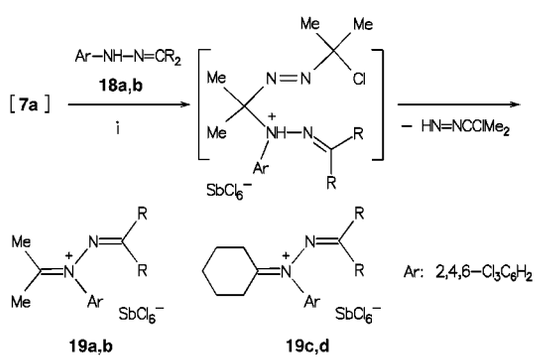
The reaction between heterocumulene **7a** and the hydrazones **18a**,**b** took a different course (Scheme 5). The azinium salts **19a**,**b** were isolated in moderate yields. Correspondingly, salt **7b** furnished the iminium salts **19c**,**d**. The ^{13}C NMR spectra of these compounds are characterized by a C=N resonance between 175 and 185 ppm and a $C{=}N^+$ signal around 200 ppm. Only occasionally have azinium salts been mentioned in the literature.[21–24] Such 2-azonia-3-azabutadienes might be of interest as dienes for Diels–Alder reactions.

Azomethines are N-alkylated by heteroallenes **3**, **7**. Similar reactions were observed for a few other N-nucleophiles (Scheme 6). With benzotriazole two equivalents of the heteroallenes **7a**,**b** reacted to afford azo compounds **20a**,**b** (85,66%) (Scheme 6). Diagnostic for the structures are the symmetries of the NMR spectra.

With the aziridine **21**, the heterocumulene **3a** reacted to



Scheme 4 *Reagents and conditions*: i, CH_2Cl_2, −70 °C to −50 °C, 30 min, **14a** 70%, **14b** 88%, **15** 69%; ii, CH_2Cl_2, reflux, 1 h, 57%; iii, CH_2Cl_2, −70 °C to +23 °C, 1 h, 74%.



Scheme 5 *Reagents and conditions*: i, CH_2Cl_2, −70 °C to −50 °C, 30 min, 23 °C, 12 h, **a** R = Me, 83%, **b** R = Ph, 77%, **c** R = Me, 61%, **d** R = Ph, 50%.

give the adduct **22** (71%). Since for this compound structural elucidation by means of NMR spectroscopy alone remained ambigous, X-ray crystallographic analysis was carried out (Fig. 1, Table 1). Included in the tables are results of semiempirical AM1 calculations.[26] X-Ray structural data for aziridinium salts seem to be unreported in the literature.

In the light of the aforementioned results it was unexpected that reactions of cumulenes **7a**–**c** with the azirine **23**, which may be regarded as a cyclic azomethine, afforded cycloadducts across the C=N double bonds, namely the triazolium salts **25a**–**c** (59–76%) (Scheme 7). Neither triazolium salts **25** nor, more generally, 1,3,4-triazabicyclo[3.1.0]hexanes or -hexenes seem to be reported in the literature. To confirm the constitution of the labile triazolium salts **25** X-ray structural analysis was carried out for **25a** (Fig. 2, Table 2).

According to AM1 calculations and in agreement with the experiments described above the bicyclic salts **25** are formed in

Table 1 Selected bond lengths (pm), bond angles and torsional angles (°) for **22**[25,26]

Atoms	Found	Calc. (AM1)	Atoms	Found	Calc. (AM1)
N1–N2	122.2(7)	122.1	C10–C13–N3	60.6(4)	59.5
N2–C7	147.8(7)	150.2	C14–C13–C15	111.6(5)	110.6
C7–N3	150.9(7)	151.7	C2–C1–N1–N2	−68.3(8)	−65
N3–C10	152.2(7)	150.2	C1–N1–N2–C7	174.6(5)	177
N3–C13	151.8(7)	150.6	N1–N2–C7–N3	168.9(5)	172
C10–C13	149.6(8)	151.9	N1–N2–C7–C8	−76.5(6)	−70
C1–N1–N2	113.1(5)	119.6	N2–C7–N3–C10	−46.9(7)	−47
N1–N2–C7	112.5(5)	117.4	N2–C7–N3–C13	34.4(7)	34
N2–C7–N3	107.8(4)	109.6	C7–N3–C10–C11	−127.7(6)	−130
C7–N3–C10	130.5(4)	128.7	C7–N3–C13–C14	−6.3(8)	−6
C7–N3–C13	131.2(4)	129.3	C7–N3–C13–C15	129.0(6)	131
C10–N3–C13	59.0(3)	60.7	N3–C13–C15–C16	−47.9(7)	−54

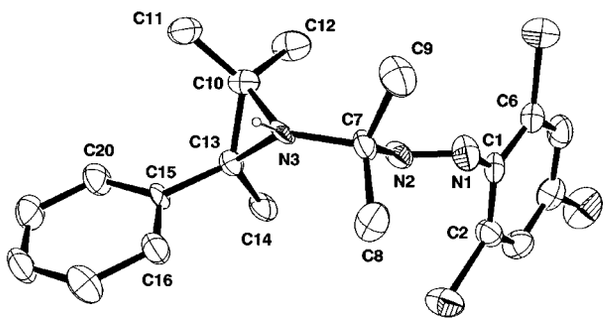
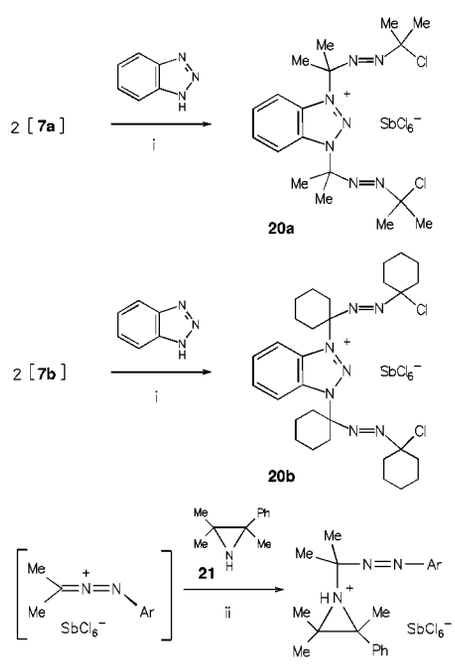


Fig. 1 ORTEP Plot of the cation **22**.



Scheme 6 *Reagents and conditions*: i, CH_2Cl_2, −70 °C to −50 °C, 30 min, 23 °C, 1 h, **20a** 85%, **20b** 66%; ii, CH_2Cl_2, −60 °C to +23 °C, 130 min, 71%. Ar = 2,4,6-$Cl_3C_6H_2$.

two steps. Concerted cycloadditions, whether synchronous or asynchronous, were calculated to have transition structures of unfavourably high energies. In the first step the azirine is N-alkylated by the heterocumulenes **7**, in analogy to N-alkylations of other imines. However, in contrast to the iminium salts described above, the azirinium ion **24** is electrophilic enough to close the ring by attack on an azo nitrogen atom. Attempts to hydrolyze compounds **25** to electrically neutral bicyclic triazoles resulted in complete decomposition.

A hint of what kind of transformations compounds **25** might undergo came from the reaction of **3a** with the azirine **23**. The

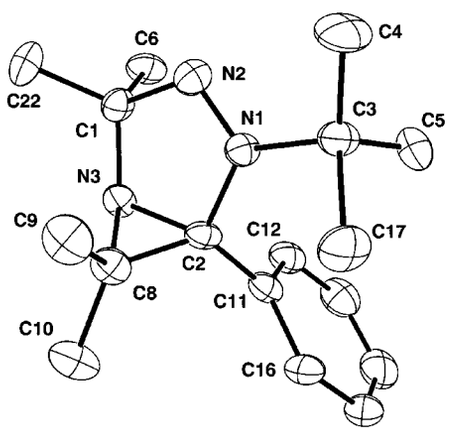
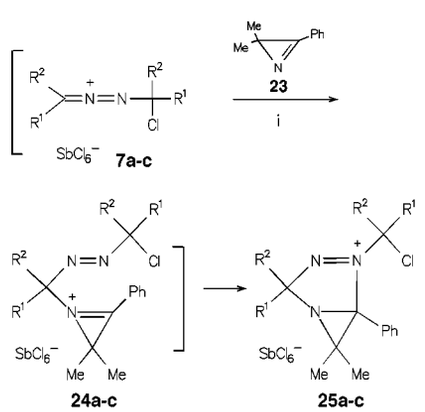


Fig. 2 ORTEP Plot of the cation **25a**.



Scheme 7 *Reagents and conditions*: i, CH_2Cl_2, −60 °C to +23 °C, 130 min, **a**, R^1, R^2 = Me, 76%, **b**, R^1–C–R^2 = $(CH_2)_5C$, 76%, **c**, R^1 = Me, R^2 = Pr^i, 59%.

triazolium salt **27** was obtained in 62% yield. A mechanistic rationale supported by AM1 calculations for the formation of compound **27** is outlined in Scheme 8. According to AM1 calculations, the opening of the two rings of compound **25d** to form the intermediate 2-azoniaallene salt **26** is a concerted process.[27–30]

The structure of the triazolium salts **27** was secured by X-ray crystallographic analysis (Fig. 3, Table 3).

Experimental

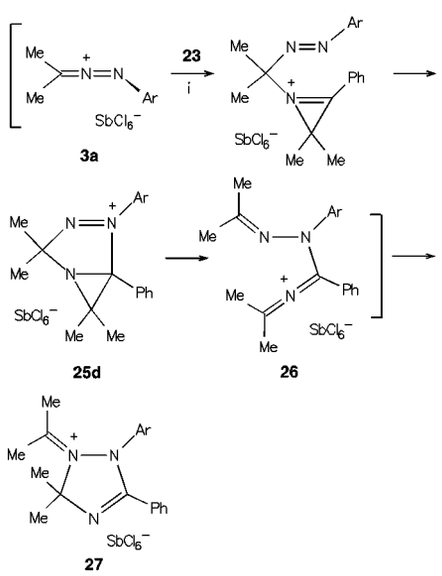
Solvents were dried by standard methods. Cycloadditions were carried out with exclusion of moisture. IR spectra: Perkin-Elmer FTIR 1600 spectrometer. ^1H and ^{13}C NMR spectra: Bruker AC-250 and WM-250 spectrometers; internal reference $SiMe_4$; 295 K; δ scale; J-values are given in Hz.

Table 2 Selected bond lengths (pm), bond angles and torsional angles (°) for **25a**[25,26]

Atoms	Found	Calc. (AM1)	Atoms	Found	Calc. (AM1)
N1–N2	124.9(6)	123.8	C9–C8–C10	113.1(5)	109.9
N2–C1	149.4(7)	154.8	N1–N2–C1–N3	9.4(5)	4
C1–N3	145.0(7)	148.9	N2–C1–N3–C2	−10.9(5)	−10
N3–C2	146.9(6)	149.2	C1–N3–C2–N1	8.3(5)	9
C2–N1	151.9(6)	155.4	N3–C2–N1–N2	−2.6(5)	−5
N3–C8	149.6(6)	147.9	C2–N1–N2–C1	−4.2(6)	1
C2–C8	150.2(7)	149.6	N2–C1–N3–C8	55.0(6)	60
N1–N2–C1	108.3(4)	110.9	N2–N1–C2–C8	−65.2(5)	−70
N2–C1–N3	106.7(4)	108.7	N2–N1–C2–C11	137.2(5)	133
C1–N3–C2	107.4(4)	112.4	N1–N2–C1–C6	−107.2(5)	−114
N3–C2–N1	101.9(4)	105.1	N1–C2–C8–C9	−20.9(7)	−26
C2–N1–N2	114.6(4)	112.3	N1–C2–C11–C12	−79.8(6)	−77
N3–C2–C8	60.5(3)	61.4	C1–N2–N1–C3	176.9(4)	180
C2–N3–C8	60.9(3)	61.8	N2–N1–C3–C4	14.2(7)	22

Table 3 Selected bond lengths (pm), bond angles and torsional angles (°) for **27**[25,26]

Atoms	Found	Calc. (AM1)	Atoms	Found	Calc. (AM1)
N1–N2	142.3(3)	140.6	N1–C1–C14	119.0(2)	119.8
N2–C2	156.5(3)	159.5	N1–N2–C2–N3	−4.4(3)	−9
C2–N3	145.1(4)	147.9	N2–C2–N3–C1	1.1(3)	5
N3–C1	126.5(3)	130.8	C2–N3–C1–N1	2.7(3)	1
C1–N1	142.0(3)	149.3	N3–C1–N1–N2	−5.6(3)	−7
N1–N2–C2	105.7(2)	107.1	C1–N1–N2–C2	5.7(2)	9
N2–C2–N3	103.0(2)	103.1	N1–N2–C5–C6	−179.3(4)	−175
C2–N3–C1	110.0(2)	109.6	N1–N2–C2–C3	−120.8(2)	−129
N3–C1–N1	115.9(2)	114.3	N1–N2–C2–C4	111.4(3)	109
C1–N1–N2	105.3(2)	105.1	N2–N1–C8–C9	−71.0(3)	−63
N1–N2–C5	125.4(2)	124.6	N1–C1–C14–C15	−127.0(3)	−131
N2–N1–C8	122.8(2)	118.7	C5–N2–N1–C8	−38.9(4)	−51



Scheme 8 *Reagents and conditions*: i, CH_2Cl_2, −60 °C to +23 °C, 130 min, 62%, Ar: 2,4,6-$Cl_3C_6H_2$.

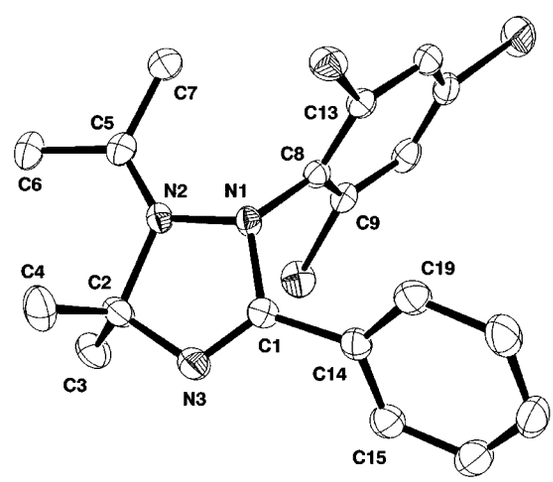


Fig. 3 ORTEP Plot of the cation **27**. The crystal of **27** contained two independent cations and anions with very similar bonding parameters. Fig. 3 shows one of the independent cations, and in Table 3 data for this cation are presented.

X-Ray structural analysis of 22[25]

Crystal data. $[C_{20}H_{23}Cl_3N_3]^+[SbCl_6]^-$, $M = 746.2$, monoclinic, space group $P2_1/n$ (No. 14), $a = 1064.7(2)$, $b = 2351.4(2)$, $c = 1256.3(2)$ pm, $\beta = 112.67(2)°$, $T = 153$ K, $V = 2902(1) \times 10^6$ pm^3, $Z = 4$, $F(000) = 1472$, $D_c = 1.708$ g cm^{-3}, μ(Mo-Kα) = 17.95 cm^{-1}, $\lambda = 71.069$ pm.

Data collection. Intensity data were collected on an Enraf-Nonius CAD4 four-circle diffractometer using Mo-Kα radiation from a graphite monochromator in the θ-range of 1.73–26.98° with a scan width in ω of 1.00° + 0.35 tan θ. The crystal used had dimensions 0.4 × 0.4 × 0.3 mm. Three reference reflections were measured every 1 h which showed a decrease of 5.2% in intensities throughout data collection. Both a linear intensity correction and a semiempirical absorption correction from ψ-scans were applied. Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 5147 unique reflections with $I/\sigma(I) > 2$ (R_{int} = 0.067 for all 6326 reflections).

Structure solution and refinement.[31] The structure was solved by the Patterson method. All the non-hydrogen and 19 of the hydrogen atoms were located by difference-Fourier synthesis. The remaining four hydrogen atoms were fixed in calculated positions [d(C–H) = 0.95 pm]. The final cycles of full-matrix least-squares refinement converged against $R = 0.0572$ and $wR(F^2) = 0.1434$ for 298 parameters and 5148 reflections with

$I/\sigma(I) > 2$ with weights of $1/[\sigma^2(F_o^2) + 0.0780p^2 + 25.82p]$ where $p = [\max(F_o^2,0) + 2F_c^2]/3$. In the final difference-Fourier map there were relatively high residual peaks in the range of -1.98 to 2.41×10^{-6} e pm^{-3}. The highest peaks resulted from a non resolved disorder of one of the $SbCl_6^-$ ions. Resolution of the disorder did not lead to significantly improved R indices. The other peaks and holes were located within 90 pm around Sb1 resulting from absorption effects and ghost peaks of the Fourier synthesis.

X-Ray structural analysis of 25a[25]

Crystal data. $[C_{16}H_{23}ClN_3]^+[SbCl_6]^-$, $M = 627.3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 895.3(2)$, $b = 1682.6(1)$, $c = 1668.6(3)$ pm, $\beta = 101.5(1)°$, $T = 153$ K, $V = 2463(1) \times 10^6$ pm^3, $Z = 4$, $F(000) = 1240$, $D_c = 1.691$ g cm^{-3}, μ(Mo-Kα) = 18.9 cm^{-1}, $\lambda = 71.069$ pm.

Data collection. Intensity data were collected on an Enraf-Nonius CAD4 four-circle diffratometer using Mo-Kα radiation from a graphite monochromator in the θ-range of 1.74–26.95° with a scan width in ω of 0.90° + 0.35 tan θ. The crystal used had dimensions 0.4 × 0.3 × 0.2 mm. Three reference reflections were measured every 1 h. Because of partial decomposition of the crystal during the data collection, the data set was divided into three parts. The decay in intensities of the first part of the data amounted to 13.3%, for the second part to 27.8%, and to 4.6% for the third part. Each part was corrected assuming linear decomposition and was scaled independently in the program SHELX-97. Lorentz and polarization corrections were applied to the data. No absorption corrections were applied to the data. No absorption corrections could be applied. Finally, 5683 reflections were collected to give 4613 unique reflections with $I/\sigma(I) > 2$ ($R_{int} = 0.000$ for all 5683 reflections).

Structure solution and refinement.[31] The structure was solved by the Patterson method. All the non-hydrogen and eight of the hydrogen atoms were located by difference-Fourier synthesis. The other hydrogen atoms were fixed in calculated positions [d(C–H) = 95 pm]. The final cycles of full-matrix least-squares refinement converged against $R = 0.0632$ and $wR(F^2) = 0.1869$ for 246 parameters with weights of $1/[\sigma^2(F_o^2) + 0.106p^2 + 1.68p]$ where $p = [\max(F_o^2, 0) + 2F_c^2]/3$. In the final difference-Fourier map there are relatively high residual peaks in the range of -2.64 to 1.84×10^{-6} e pm^{-3}. These peaks result from absorption effects because an absorption correction for the data of the decomposing crystal could not be applied. The residual peaks are definitively not caused by cocrystallized solvent because there are no voids in the structure large enough to contain diffuse solvent molecules. The $SbCl_6^-$ ion is slightly disordered causing electron density in a sphere around Sb. It was not considered worthwhile to resolve this disorder.

X-Ray structural analysis of 27[25]

Crystal data. $[C_{19}H_{19}Cl_3N_3]^+[SbCl_6]^-$, $M = 730.2$, monoclinic, space group $P2_1/a$ (No. 14), $a = 1487.7(5)$, $b = 1354.2(1)$, $c = 2872.9(7)$ pm, $\beta = 104.5(1)°$, $T = 153$ K, $V = 5604(2) \times 10^6$ pm^3, $Z = 8$, $F(000) = 2864$, $D_c = 1.731$ g cm^{-3}, μ(Mo-Kα) = 18 cm^{-1}, $\lambda = 71.069$ pm.

Data collection. Intensity data were collected on an Enraf-Nonius CAD4 four-circle diffractometer using Mo-Kα radiation from a graphite monochromator in the θ-range of 1.67–27.41° with a scan width in ω of 0.80° + 0.35 tan θ. The yellow crystal used had dimensions 0.5 × 0.4 × 0.3 mm. Three reference reflections were measured every 1 h which showed no significant variation in intensities throughout data collection. Absorption corrections from ψ-scans as well as Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 10548 unique reflections with $I/\sigma(I) > 2$ ($R_{int} = 0.014$ for all 13217 reflections).

Structure solution and refinement.[31] The structure was solved by the Patterson method. All the non-hydrogen and hydrogen atoms were located by difference-Fourier synthesis. The unit cell of **27** contained two independent cations as well as two independent anions with similar geometrical parameters. The final cycles of full-matrix least-squares refinement converged against $R = 0.0293$ and $wR(F^2) = 0.0650$ for 729 parameters with weights of $1/[\sigma^2(F_o^2) + 0{,}0244p^2 + 8.08p]$ where $p = [\max(F_o^2,0) + 2F_c^2]/3$. In the final difference-Fourier map there were no residual peaks outside the range -0.74 to 0.52×10^{-6} e pm^{-3}.

Benzylidene-*N*-[1-(1-chloro-1-methylethylazo)-1-methylethyl]-*N*-methylammonium hexachloroantimonate 10a

The reactive intermediate **7a** was prepared by addition of a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) to a cold (−70 °C) suspension of 1,1′-dichloro-1,1′-dimethylazoethane **6a**[7,11,12] (1.83 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring for 5 min a solution of benzylidenemethylamine[32] (1.19 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise. Stirring between −70 and −50 °C was continued for 30 min. Et_2O (100 ml) was added dropwise and the mixture was stirred at −30 °C for a further 15 min. Filtration afforded a powder (4.60 g, 77%), which was reprecipitated at 0 °C from CH_2Cl_2 (20 ml)–Et_2O (20 ml) to furnish *title compound* **10a** as a very moisture sensitive powder (3.50 g, 58%), for which a correct elemental analysis could not be obtained; mp 108–110 °C (decomp.) (Found: C, 27.27; H, 3.47; N, 6.32. $C_{14}H_{21}Cl_7N_3Sb$ (MW = 601.3) requires C, 27.97; H, 3.52; N, 6.99%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1596, 1634; δ_H(250 MHz; CD_3CN) 1.80 (6 H), 1.88 (6 H) and 3.85 (d, J 0.9, 3 H) (CH_3), 7.34–8.06 (m's, phenyl), 9.22 (br, =CH); δ_C(62.9 MHz; CD_3CN; 263 K) 24.3 (2 C), 30.1 (2 C) and 41.0 (CH_3), 95.0 and 96.1 (C–N), 128.1, 130.7, 134.8 and 137.6 (phenyl), 172.7 (C=N).

Benzylidene-*N*-[1-(1-chloro-1-methylethylazo)-1-methylethyl]-*N*-isopropylammonium hexachloroantiomonate 10b

Compound **10b** was prepared from benzylideneisopropylamine[33,34] (1.47 g, 10 mmol) in the manner described for **10a**. The very moisture sensitive *title compound* **10b** was isolated as a powder (5.59 g, 89%), which decomposed on attempted reprecipitation and for which a correct elemental analysis could not be obtained; mp 103–105 °C (decomp.) (Found: C, 29.61; H, 4.00; N, 6.01. $C_{16}H_{25}Cl_7N_3Sb$ (MW = 629.3) requires C, 30.53; H, 4.00; N, 6.68); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1739; δ_H(250 MHz; CD_2Cl_2; 273 K) 1.79 (d, J 6.9, 6 H) and 1.95 (12 H) (CH_3), 5.15 (septet, J 6.9, CH), 7.74–7.95 (phenyl), 9.31 (=CH); δ_C(62.9 MHz; CD_2Cl_2; 273 K; partial decomposition during data collection) 22.6, 28.6 (br) and 30.3 (CH_3), 61.2 (CH), 94.8 and 99.0 (C–N), 127.1, 130.6, 132.5 and 137.1 (phenyl), 173.4 (br, C=N).

1-[1-(1-Chloro-1-methylethylazo)-1-methylethyl]-4,5-dihydro-2-methoxy-3*H*-pyrrol-1-ium hexachloroantimonate 12

Compound **12** was prepared from 4,5-dihydro-2-methoxy-3*H*-pyrrole[35] **11** (1.00 g, 10 mmol) in the manner described for **10a**. A powder (5.52 g, 95%) was isolated, which was stirred at −20 °C in CH_2Cl_2 (30 ml). After addition of Et_2O (20 ml) the mixture was left at −20 °C for 12 h. Filtration afforded the *title compound* **12** as a moisture sensitive crystalline powder (5.10 g, 88%); mp 90–93 °C (decomp.) (Found: C, 22.34; H, 3.68; N, 7.18. $C_{11}H_{21}Cl_7N_3OSb$ (MW = 581.2) requires C, 22.73; H, 3.64; N, 7.23%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1629, 1665; δ_H(250 MHz; CD_3CN) 1.65 (6 H), 1.82 (6 H) and 4.19 (3 H) (CH_3), 2.30 (quintet, J 8.3, 2 H), 3.23 (t, J 8.4, 2 H) and 4.07 (m, 2 H) (CH_2);

δ_C(62.9 MHz; CD_3CN) 18.0, 23.8 (2 C), 30.2 (2 C), 31.6, 54.0, 64.3, 88.5 and 93.8 (CH_3, CH_2, C–N), 183.6 (C=N).

1,1′-Dimethyl-1,1′-bis(4,5-dihydro-2-methoxy-3*H*-pyrrol-1-ium-1-yl)azoethane dihexachloroantimonate 13

Compound **13** was prepared from pyrrole **11** (1.98 g, 20 mmol), the azo compound **6a** (1.83 g, 10 mmol) and $SbCl_5$ (5.98 g, 20 mmol) in the manner described for **10a**. Filtration afforded a yellow powder (9.24 g, 94%), which was stirred at 23 °C in CH_2Cl_2 (80 ml) for 1 h. Filtration furnished *title compound* **13** as a moisture sensitive pale yellow powder (8.08 g, 83%), for which a correct elemental analysis could not be obtained; mp 138–140 °C (decomp.) (Found: C, 19.15; H, 3.10; N, 5.28. $C_{16}H_{30}Cl_{12}N_4O_2Sb_2$ (MW = 979.4) requires C, 19.62; H, 3.09; N, 5.72%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1635, 1599; δ_H(250 MHz; CD_3CN) 1.63 (12 H, CH_3), 4.21 (6 H, OCH_3), 2.32 (m, 4 H), 3.25 (t, *J* 8.3, 4 H) and 4.08 (t, *J* 7.6, 4 H) (CH_2); δ_C(62.9 MHz; CD_3CN) 18.0, 23.8, 31.7, 54.1, 64.6 and 88.9 (CH_2, OCH_3, C–N), 183.8 (C=N).

1,4-Dihydro-1,1,4,4-tetramethylpyrazolo[1,2-*a*][1,2,4,5]tetrazin-5-ium hexachloroantimonate 14a

Compound **14a** was prepared from pyrazole (0.68 g, 10 mmol), the azo compound **6a** (1.83 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **10a**, except that the reaction mixture was stirred at 23 °C for 6 h. After cooling to −20 °C and addition of Et_2O (120 ml) a pale yellow powder (4.20 g, 82%) was isolated by filtration. Crystallization at −20 °C from MeCN (10 ml)–CH_2Cl_2 (30 ml)–Et_2O (20 ml) afforded *title compound* **14a** as a crystalline powder (3.60 g, 70%); mp 118–120 °C (decomp.) (Found: C, 20.95; H, 2.89; N, 10.71. $C_9H_{15}Cl_6N_4Sb$ (MW = 513.7) requires C, 21.04; H, 2.94; N, 10.91%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3159, 3144, 3124, 1594; δ_H(250 MHz; CD_3CN) 2.03 (4 CH_3), 7.08 (t, *J* 3.1, 1 H) and 8.42 (d, *J* 3.1, 2 H) (=CH); δ_C(62.9 MHz; CD_3CN) 28.0 (CH_3), 82.5, 110.4 and 135.5 (NCN, =CH).

Cyclohexanespiro-1′-(1′,4′-dihydropyrazolo[1,2-*a*][1,2,4,5]-tetrazin-5′-ium)-4′-spirocyclohexane hexachloroantimonate 14b

Compound **14b** was prepared from pyrazole (0.68 g, 10 mmol), 1,1′-dichloroazocyclohexane **6b**[7,11,12] (2.63 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **10a**. The *title compound* **14b** was isolated by filtration as a crystalline powder (5.20 g, 88%), which could be recrystallized at −20 °C from MeCN (20 ml)–CH_2Cl_2 (40 ml) to afford a crystalline powder; mp 122–124 °C (decomp.) (Found: C, 30.44; H, 3.98; N, 9.49. $C_{15}H_{23}Cl_6N_4Sb$ (MW = 593.8) requires C, 30.34; H, 3.90; N, 9.44%); ν_{max}(Nujol)/cm^{-1} 3151; δ_H(250 MHz; CD_3CN) 1.64–2.35 (m's, 20 H, CH_2), 7.06 (t, *J* 3.1, 1 H) and 8.42 (d, *J* 3.1, 2 H) (=CH); δ_C(62.9 MHz; CD_3CN) 23.2 (4 C), 25.1 (2 C) and 39.2 (4 C, CH_2), 84.6, 110.2 and 135.1 (NCN, =CH).

2- (or 1-)[1-(1-Chloro-1-methylethylazo)-1-methylethyl]-1*H*-indazol-2-ium hexachloroantimonate 15

Compound **15** was prepared from 1*H*-indazole (1.18 g, 10 mmol), the azo compound **6a** (1.83 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **10a**, except that the reaction mixture was stirred at 23 °C for 4 h. After cooling to −20 °C and slow addition of Et_2O (120 ml) the mixture was stirred at −20 °C for 1 h. The *title compound* **15** was isolated by filtration as a powder (4.82 g, 80%). Crystallization at −20 °C from CH_2Cl_2 (40 ml)–Et_2O (10 ml) afforded yellow needles (4.16 g, 69%); mp 108–110 °C (decomp.) (Found: C, 25.75; H, 3.16; N, 9.28. $C_{13}H_{18}Cl_7N_4Sb$ (MW = 600.2) requires C, 26.01; H, 3.02; N, 9.34%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1636; δ_H(250 MHz; CD_3CN) 1.82 (6 H) and 2.07 (6 H) (CH_3), 7.55–8.13 (m's, 4 H) and 9.02 (d, *J* 1.0, 1 H) (aryl), 12.39 (br, NH); δ_C(62.9 MHz; CD_3CN) 25.1 (2 C) and 30.1 (2 C) (CH_3), 92.1 and 94.0 (C–N), 112.5, 120.9, 124.0, 126.8, 132.9, 135.6 and 141.6 (aryl).

1,4-Dihydro-1,1,4,4-tetramethylindazolo[1.2-*a*][1,2,4,5]tetrazin-5-ium hexachloroantimonate 16

A solution of **15** (3.00 g, 5 mmol) in CH_2Cl_2 (20 ml) was boiled under reflux for 1 h. After addition of Et_2O (20 ml) the mixture was kept at −15 °C for 1 h. Filtration afforded a powder (2.60 g, 92%), which was crystallized at −15 °C from CH_2Cl_2 (20 ml)–Et_2O (5 ml) to furnish *title compound* **16** as a crystalline powder (1.60 g, 57%); mp 124–126 °C (decomp.) (Found: C, 27.64; H, 3.05; N, 9.97. $C_{13}H_{17}Cl_6N_4Sb$ (MW = 563.8) requires C, 27.69; H, 3.04; N, 9.94%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1627; δ_H(250 MHz; CD_3CN; 273 K) 2.14 (6 H) and 2.16 (6 H) (CH_3), 7.64–8.22 (m's, 4 H) and 9.15 (d, *J* 0.8, 1 H) (=CH); δ_C(62.9 MHz; CD_3CN; 273 K) 26.3 (2 C) and 28.2 (2 C) (CH_3), 82.0 and 84.0 (C–N), 114.0, 120.5, 124.9, 127.5, 132.3, 135.8 and 140.4 (=C).

1,3-Bis[1-(1-chloro-1-methylethylazo)-1-methylethyl]benzimidazolium hexachloroantimonate 17

A solution of $SbCl_5$ (1.50 g, 5 mmol) in CH_2Cl_2 (20 ml) was added to a cold (−70 °C) suspension of the azo compound **6a** (1.83 g, 10 mmol) and benzimidazole (0.59 g, 5 mmol) in CH_2Cl_2 (40 ml). After stirring at −70 °C for 30 min, then at 23 °C for 1 h, Et_2O (120 ml) was added and the mixture was left at −15 °C for 12 h. Isolation by filtration afforded *title compound* **17** as a powder (2.96 g, 79%). Recrystallization at −15 °C from CH_2Cl_2 (20 ml) furnished a crystalline powder (2.78 g, 74%); mp 168–170 °C (decomp.) (Found: C, 30.25; H, 3.84; N, 10.80. $C_{19}H_{29}Cl_8N_6Sb$ (MW = 746.9) requires C, 30.55; H, 3.91; N, 11.26%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1603, 1547; δ_H(250 MHz; CD_3CN) 1.86 (12 H) and 2.03 (12 H) (CH_3), 7.65–7.84 (AA′BB′ pattern, 4 H) and 9.18 (1 H) (aryl); δ_C(62.9 MHz; CD_3CN) 25.4 and 30.2 (CH_3), 89.9 and 94.7 (C–N), 118.3 (?), 128.0, 132.2 and 139.9 (=C).

1,2-Diisopropylidene-1-(2,4,6-trichlorophenyl)hydrazinium hexachloroantimonate 19a

Compound **19a** was prepared from hydrazone **18a**[1] (2.52 g, 10 mmol), the azo compound **6a** (1.83 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **10a**, except that the reaction mixture was stirred at 23 °C for 12 h. After cooling to −20 °C and slow addition of Et_2O (120 ml) the mixture was stirred at −20 °C for 1 h. The *title compound* **19a** was isolated by filtration as a powder (5.20 g, 83%). Crystallization at −20 °C from CH_2Cl_2 (40 ml)–Et_2O (20 ml) afforded fine prisms; mp 126–128 °C (decomp.) (Found: C, 22.83; H, 2.27; N, 4.52. $C_{12}H_{14}Cl_9N_2Sb$ (MW = 627.1) requires C, 22.98; H, 2.25; N, 4.47%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1627, 1612, 1573, 1560; δ_H(250 MHz; CD_3CN) 2.22, 2.29, 2.53 and 2.66 (CH_3), 7.79 (aryl); δ_C(62.9 MHz; CD_3CN), 23.5, 24.8, 25.8 and 25.9 (CH_3), 131.5, 132.7, 134.5 and 139.5 (aryl), 184.6 and 191.8 (C=N).

2-Diphenylmethylene-1-isopropylidene-1-(2,4,6-trichlorophenyl)-hydrazinium hexachloroantimonate 19b

Compound **19b** was prepared from hydrazone **18b**[1] (3.75 g, 10 mmol), the azo compound **6a** (1.83 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **19a**. The *title compound* **19b** was isolated by filtration as a yellow crystalline powder (5.80 g, 77%); mp 135–137 °C (decomp.) (Found: C, 35.39; H, 2.49; N, 3.71. $C_{22}H_{18}Cl_9N_2Sb$ (MW = 751.2) requires C, 35.17; H, 2.42; N, 3.73%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1587, 1565, 1557; δ_H(250 MHz; CD_3CN) 2.60 and 3.08 (CH_3), 7.59 (2 H, aryl), 7.01–7.68 (m's, 10 H, phenyl); δ_C(62.9 MHz; CD_3CN) 26.6 and 27.1 (CH_3), 127.8, 129.8, 130.0, 131.1, 131.2, 131.8, 132.8, 133.3, 134.8, 134.9, 136.4 and 139.5 (aryl), 175.4 and 198.9 (C=N).

1-Cyclohexylidene-2-isopropylidene-1-(2,4,6-trichlorophenyl)-hydrazinium hexachloroantimonate 19c

Compound **19c** was prepared from hydrazone **18a** (2.52 g, 10

mmol), the azo compound **6b** (2.63 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **19a**. The *title compound* **19c** was isolated by filtration as a pale yellow powder (4.60 g, 66%). Crystallization at −20 °C from CH_2Cl_2 (40 ml)–Et_2O (20 ml) afforded a crystalline powder (4.10 g, 61%); mp 130–132 °C (decomp.) (Found: C, 27.08; H, 2.85; N, 4.15. $C_{15}H_{18}Cl_9N_2Sb$ (MW = 667.1) requires C, 27.00; H, 2.72; N, 4.20%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1628, 1591, 1571, 1557; δ_H(250 MHz; CD_3CN–CD_2Cl_2 ≈ 1:1, 273 K) 2.25 and 2.28 (CH_3), 1.82 (m, 2 H), 2.04 (m's, 4 H), 2.72 (t, *J* 6.3, 2 H) and 2.91 (t, *J* 6.4, 2 H) (CH_2), 7.75 (aryl); δ_C(62.9 MHz; CD_3CN–CD_2Cl_2 ≈ 1:1, 273 K) 23.1, 24.2, 25.8, 27.9, 28.6, 33.5, 35.0 (CH_2, CH_3), 131.0 and 133.7, 139.2 (aryl), 183.7 and 195.2 (C=N).

2-Diphenylmethylene-1-cyclohexylidene-1-(2,4,6-trichlorophenyl)hydrazinium hexachloroantimonate 19d

Compound **19d** was prepared from hydrazone **18b** (3.75 g, 10 mmol), the azo compound **6b** (2.63 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in the manner described for **19a**. The product was isolated by filtration as a yellow powder (4.10 g, 55%). Crystallization at −20 °C from CH_2Cl_2 (30 ml)–MeCN (30 ml)–Et_2O (20 ml) afforded prisms (3.78 g, 50%) of the *title compound* **19d**; mp 134–136 °C (decomp.) (Found: C, 37.97; H, 2.84; N, 3.57. $C_{25}H_{22}Cl_9N_2Sb$ (MW = 791.3) requires C, 37.95; H, 2.80; N, 3.54%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1588, 1565, 1556; δ_H(250 MHz; CD_2Cl_2–CD_3CN ≈ 4:1) 1.89 (m, 2 H), 2.05 (m, 2 H), 2.69 (m, 2 H) and 3.50 (m, 2 H) (CH_2), 7.37 (2 H, aryl), 6.97–7.67 (m's, phenyl); δ_C(62.9 MHz; CD_2Cl_2–CD_3CN ≈ 4:1) 24.3, 28.6, 29.6, 35.3 and 36.2 (CH_2), 127.4, 129.5, 129.6, 130.6, 130.9, 131.7, 132.3, 132.8, 133.9, 134.7, 135.5 and 139.3 (aryl), 176.2 and 201.6 (C=N).

1,3-Bis[1-(1-chloro-1-methylethylazo)-1-methylethyl]benzotriazolium hexachloroantimonate 20a

A solution of $SbCl_5$ (1.50 g, 5 mmol) in CH_2Cl_2 (20 ml) was added to a cold (−70 °C) suspension of the azo compound **6a** (1.83 g, 10 mmol) and benzotriazole (0.60 g, 5 mmol) in CH_2Cl_2 (60 ml). After stirring at −70 °C for 30 min, then at 23 °C for 1 h, CCl_4 (120 ml) was added and the mixture was stirred at −20 °C for 1 h. Isolation by filtration afforded the *title compound* **20a** as a crystalline powder (3.18 g, 85%); mp 140–142 °C (decomp.) (Found: C, 28.55; H, 3.71; N, 12.89. $C_{18}H_{28}Cl_8N_7Sb$ (MW = 747.9) requires C, 28.91; H, 3.77; N, 13.11%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1602; δ_H(250 MHz; CD_3CN) 1.87 (6 H) and 2.14 (6 H) (CH_3), 7.91–8.21 (AA′BB′ pattern, 4 H, =CH); δ_C(62.9 MHz; CD_3CN; 273 K) 25.5 and 30.2 (CH_3), 95.1 and 95.7 (C–N), 117.7, 132.1 and 136.2 (=C).

1,3-Bis[1-(1-chlorocyclohexylazo)-1-cyclohexyl]benzotriazolium hexachloroantimonate 20b

Compound **20b** was prepared from azo compound **6b** (2.63 g, 10 mmol), benzotriazole (0.60 g, 5 mmol) and $SbCl_5$ (1.50 g, 5 mmol) in the manner described for **20a**. The *title compound* **20b** was isolated as a very moisture sensitive pale pink powder (3.38 g, 74%). Crystallization at −15 °C from CH_2Cl_2 (40 ml)–CCl_4 (10 ml) afforded needles (3.00 g, 66%); mp 138–140 °C (decomp.) (Found: C, 39.62; H, 5.10; N, 10.48. $C_{30}H_{44}Cl_8N_7$ Sb (MW = 908.1) requires C, 39.68; H, 4.88; N, 10.78%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1600; δ_H(250 MHz; CD_3CN–CD_2Cl_2 2:1, 273 K) 1.30–2.69 (m′s, 40 H, CH_2), 7.89 (m, 4 H, =CH); δ_C(62.9 MHz; CD_3CN–CD_2Cl_2 2:1, 273 K) 22.3, 22.7, 24.8, 24.9, 34.5 and 38.2 (CH_2), 96.7 and 98.3 (C–N), 117.3, 132.0 and 135.8 (=C).

[1-Methyl-1-(2,3,3,trimethyl-2-phenylaziridinium-1-yl)ethyl]-azo(2,4,6-trichlorobenzene) hexachloroantimonate 22

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (30 ml) was added dropwise to a cold (−60 °C) mixture of 2,3,3-trimethyl-2-phenylaziridine **21**[35–37] (1.61 g, 10 mmol) and (1-chloro-1-methylethyl)azo(2,4,6-trichlorobenzene) **2a**[1] (2.86 g, 10 mmol) in CH_2Cl_2 (30 ml). The mixture was stirred at −60 °C for 1 h, then at 0 °C for 1 h, and finally at 23 °C for 10 min. Pentane (100 ml) was added dropwise and the mixture was left at −15 °C for 2 h. Filtration and crystallization of the residue at −15 °C from CH_2Cl_2 (50 ml)–MeCN (6 ml)–Et_2O (80 ml) afforded *title compound* **22** as a yellow crystalline powder (5.32 g, 71%); mp 102–105 °C (decomp.). Crystals suitable for X-ray structural analysis were obtained by recrystallization at −15 °C from CH_2Cl_2–Et_2O (Found: C, 32.53; H, 3.32; N, 5.52. $C_{20}H_{23}Cl_9N_3Sb$ (MW = 746.2) requires C, 32.19; H, 3.11; N, 5.63%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1614; δ_H(250 MHz; CD_3CN; 263 K) 1.51, 1.86, 1.89, 1.92 and 2.08 (CH_3), 6.76 (br, NH), 7.43–7.58 (m′s, phenyl), 7.65 (aryl); δ_C(62.9 MHz; CD_3CN; 263 K) 16.9, 20.5, 24.4, 26.4 and 26.9 (CH_3), 60.2, 66.0 and 93.7 (C–N), 127.0, 128.0, 130.1, 130.3, 135.3, 137.1 and 146.5 (aryl).

1-(1-Chloro-1-methylethyl)-3,3,5,5-tetramethyl-5a-phenyl-5,5a-dihydro-3*H*-azireno[2,1-*c*][1,2,4]triazol-1-ium hexachloroantimonate 25a

Compound **25a** was prepared from 3,3-dimethyl-2-phenylazirine **23**[38] (1.45 g, 10 mmol) and the azo compound **6a** (1.83 g, 10 mmol) in the manner described for **22**. Crystallization at −15 °C from CH_2Cl_2 (40 ml)–Et_2O (15 ml) afforded the moderately stable *title compound* **25a** as a yellow powder (4.73 g, 76%); mp 91–94 °C (decomp.). Yellow prisms suitable for crystallographic analysis were obtained by slow crystallization at −15 °C from CH_2Cl_2–Et_2O (Found: C, 30.14; H, 3.67; N, 6.59. $C_{16}H_{23}Cl_7N_3Sb$ (MW = 627.3) requires C, 30.63; H, 3.70; N, 6.70%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1451; δ_H(250 MHz; CD_3CN; 263 K) 1.35 (br, 3 H), 1.40 (br, 3 H), 1.55 (br, 3 H), 2.03 (6 H), 2.23 (br, 3 H), 7.45–8.01 (m′s, 2 H); δ_C(62.9 MHz; CD_3CN; 263 K) 18.9 (br), 19.4 (br), 24.4 (br), 31.8 (br), 32.2 (br) and 33.1 (br) (CH_3), 51.1, 95.3, 100.3 and 107.0 (C–N), 126.8, 130.5 (br), 130.9 (br), 132.4 (br), 133.4 and 133.7 (br) (phenyl).

Cyclohexanespiro-3′-[1-(1-chlorocyclohexyl)-5,5-dimethyl-5a-phenyl-5,5a-dihydro-3*H*-azireno[2,1-*c*][1,2,4]triazol-1-ium] hexachloroantimonate 25b

Compound **25b** was prepared from the azirine **23** (1.45 g, 10 mmol) and the azo compound **6b** (2.63 g, 10 mmol) in the manner described for **22**. Crystallization at −15 °C from CH_2Cl_2 (50 ml)–Et_2O (20 ml) afforded *title compound* **25b** as a yellow crystalline powder (5.36 g, 76%); mp 80–84 °C (decomp.) (Found: C, 37.53; H, 4.86; N, 5.63. $C_{22}H_{31}Cl_7N_3Sb$ (MW = 707.4) requires C, 37.35; H, 4.94; N, 5.94%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1448; δ_H(250 MHz; CD_2Cl_2; 263 K) 1.40 (6 H, CH_3), 1.24–2.49 (m′s, 20 H, CH_2), 7.38–7.90 (br, m′s, phenyl); δ_C(62.9 MHz; CD_2Cl_2; 263 K) 19.7 (br), 20.8 (br), 22.8 (br), 22.9 (br), 23.5, 24.4 (br), 24.7, 29.3 (br), 40.1 and 41.2 (br) (CH_3, CH_2), 49.5, 99.4, 100.3 and 109.5 (C–N), 126.1, 129.9 (br), 130.4 (br), 131.4 (br), 132.8 (br) and 132.9 (phenyl).

1-(1-Chloro-1,2-dimethylpropyl)-3-isopropyl-3,5,5-trimethyl-5a-phenyl-5,5a-dihydro-3*H*-azireno[2.1-*c*][1,2,4]triazol-1-ium hexachloroantimonate 25c

Compound **25c** was prepared from the azirine **23** (1.45 g, 10 mmol) and the azo compound **6c**[7,14,17] (2.39 g, 10 mmol) in the manner described for **22**. Crystallization at −15 °C from CH_2Cl_2 (35 ml)–Et_2O (15 ml) afforded *title compound* **25c** as a yellow crystalline powder (3.97 g, 59%); mp 78–82 °C (decomp.) (Found: C, 33.96; H, 4.41; N, 5.61. $C_{20}H_{31}Cl_7N_3Sb \cdot \frac{1}{2}$ CH_2Cl_2 (MW = 725.9) requires C, 33.92; H, 4.44; N, 5.79%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1464; δ_H(250 MHz; CD_2Cl_2; 263 K) 0.71 (d, *J* 6.7, 3 H), 1.05 (d, *J* 6.7, 3 H), 1.37 (3 H), 1.39 (d, *J* ≈ 6.5, 3 H), 1.42 (d, *J* ≈ 6, 3 H), 1.42 (3 H), 1.90 (3 H) and 2.06 (br, 3 H) (CH_3), 1.51 (m, 1 H) and 2.03 (m, 1 H) (CH), 7.36–7.98 (m′s, phenyl);

δ_C(62.9 MHz; CD_2Cl_2; 263 K) 12.2 (br), 16.5, 16.7, 16.9, 18.0, 20.0 (br), 24.4 (br) and 25.7 (br) (CH_3), 39.3 and 44.8 (br) (CH), 50.7, 100.3, 103.1 and 112.2 (C–N), 125.2, 129.9, 130.3, 130.7, 133.0 and 133.2 (phenyl).

2,3-Dihydro-2-isopropylidene-3,3-dimethyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate 27

Compound **27** was prepared from the azirine **23** (1.45 g, 10 mmol) and the azo compound **2a** (2.86 g, 10 mmol) in the manner described for **22**. Crystallization at −15 °C from CH_2Cl_2 (35 ml)–Et_2O (25 ml) afforded *title compound* **27** as yellow needles (4.51 g, 62%); mp 113–116 °C (decomp.). Crystals suitable for X-ray structural analysis were obtained by recrystallization at −15 °C from CH_2Cl_2–Et_2O (Found: C, 31.05; H, 2.68; N, 5.72. $C_{19}H_{19}Cl_9N_3Sb$ (MW = 730.2) requires C, 31.25; H, 2.62; N, 5.75%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1680; δ_H(250 MHz; CD_3CN; 263 K) 2.13 (3 H), 2.17 (6 H) and 2.80 (3 H) (CH_3), 7.37–7.64 (m′s, 7 H, aryl); δ_C(62.9 MHz; CD_3CN; 263 K) 25.9, 27.5 and 27.9 (2 C) (CH_3), 106.3 (C–N), 126.4, 128.9, 129.8, 131.2, 131.5, 133.3, 137.9 and 139.6 (aryl), 155.7 and 174.4 (C=N).

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