Derivatives of the Triaminoguanidinium Ion, 1. Synthesis, Crystal and Molecular Structures of 1,2,3-Tris(benzylamino)guanidinium Salts

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

Triaminoguanidinium chloride was transformed into 1,2,3-tris(benzylamino)guanidinium chloride (**3-Cl**) in two steps. Anion exchange allowed the preparation of further salts **3-X**. The crystal and molecular structures of **3-Cl**, **3-I**, **3-CF₃COO** and **3-CF₃SO₃** were determined. It was found that both the conformation of the cation and the nature of the anion determines the packing in the solid state. Interestingly, three different conformations of the cation were observed in the crystals.

Introduction

Triaminoguanidinium chloride (**1**) is readily prepared by the reaction of guanidinium chloride [1, 2], aminoguanidinium hydrogencarbonate [3], cyanogen chloride [4] or dicyanamide [1] with hydrazine hydrate. Although salt **1** was first described as early as 1904 by R. Stollé [5], the chemistry of this and other interesting multifunctional triaminoguanidinium salts began to be developed only sixty years later. Deprotonation of **1** with liquid NH_3 gave triaminoguanidine [6]. Trisarylidene- and trisalkylideneaminoguanidinium salts were obtained by reaction with aldehydes and ketones [5, 7]. Cyclization occurred upon heating of salt **1** with carboxylic acids and yielded 4-amino-3-hydrazino-1,2,4-triazoles [3, 8]; however, an analogous transformation could not be achieved with triethyl orthoacetate [3]. The reaction with pentane-2,4-dione followed by oxidation leads to a 3,6-bis(pyrazol-1-yl)-1,2,4,5-tetrazine [9]; this compound as well as other tetrazines derived therefrom have recently found some attention due to their fluorescence properties [10]. Cyclocondensation with 1,1,1-trifluoro-2,4-pentanedione follows a somewhat differ-

ent pathway [11]. The reactions of triaminoguanidinium chloride or nitrate with cyanogen bromide [12], CS_2/NaOH [12], and isothiocyanates [13] afford differently substituted 1,2,4-triazole derivatives.

The nitrogen-rich parent triaminoguanidinium ion currently meets increased attention as a constituent of energetic salts [14]. Klapötke and coworkers went a step further when they converted salt **1** by diazotization into azido derivatives which then were cyclized to give energetic and highly sensitive azidotetrazoles [15].

The multiple coordination sites of 1,2,3-tris(hydroxybenzylidene)guanidine [16] and 1,2,3-tris(α-hydroxyiminoalkyl)guanidine [17] ligands prepared from **1** have recently been used for the construction of novel metal complexes, some of which display impressive supramolecular architectures.

As a consequence of our studies on hexaalkylguanidinium salts as ionic liquids [18], we became interested in the triaminoguanidinium ion as a starting material and molecular platform for novel ionic liquids. In the course of our synthetic efforts, we also prepared 1,2,3-tris(benzylamino)guanidinium salts and wondered whether the molecular C_3 topology of the

cation would also appear in the solid state of these salts. The results of these studies are reported herein.

Results and Discussion

Syntheses

Triaminoguanidinium chloride (**1**) was transformed quantitatively into 1,2,3-tris(benzyliminyl)guanidinium chloride (**2**) by the reaction with benzaldehyde in hot aqueous ethanol (Scheme 1). Catalytic hydrogenation of **2** in dry methanol afforded in good yield (78 %) 1,2,3-tris(benzylamino)guanidinium chloride (**3-Cl**), which was well soluble in DMSO and chloroform at room temperature and in hot acetonitrile.

Other salts of **3** were obtained by anion exchange reactions of **3-Cl** (Scheme 1). Thus, anion metathesis reactions with silver trifluoroacetate, triflate or tetrafluoroborate gave salts **3-TFA**, **3-OTf** and **3-BF₄**, respectively. The iodide salt **3-I**, on the other hand, was first

obtained unintentionally, when **3-Cl** was treated with methyl iodide and triethylamine in boiling acetonitrile. Instead of the expected *N*-methylation of **3-Cl**, nucleophilic substitution of CH_3I by Cl^- took place, and salt **3-I** was isolated after workup. This reaction course, on the other hand, does not require the presence of a base, and in fact, the anion exchange also worked well in the absence of triethylamine. ^1H and ^{13}C NMR spectra of the 1,2,3-tris(benzylamino)guanidinium salts **3** confirm the C_3 molecular topology of the cation. The melting points of salts **3-Cl**, **3-I**, **3-TFA**, and **3-BF₄** are well above 100 °C. Only **3-OTf** has a melting point (109 °C), which comes close to the generally accepted definition range for an ionic liquid (*i. e.*, melting points below about 100 °C). Significantly lower melting points should result when the NH groups are replaced by *N*-alkyl groups, and when the cation is made unsymmetrical. Synthetic work along these guidelines is underway.

The thermal behavior of salt **2** deserves a note. When Stollé first reported the derivatization of **1** to
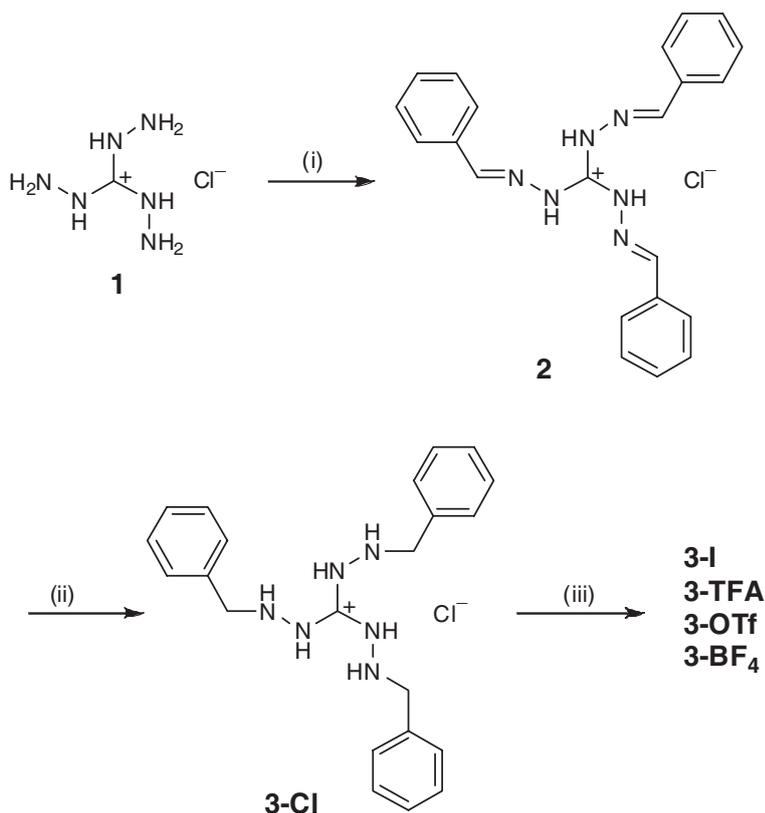
Scheme 1. Reaction conditions: (i) Ph-CHO, EtOH-H_2O (2 : 1), 80 °C, 1 – 2 h; (ii) H_2, Pd/C (cat.), methanol; (iii) CH_3I, acetonitrile, 80 °C, 20 h (**3-I**), Ag(O_2CCF_3) (**3-TFA**) or AgOTf (**3-OTf**), chloroform, 15 – 16 h; AgBF₄, CH_2Cl_2, 20 h (**3-BF₄**).

give **2** [5], he mentioned that crystallization of **2** from ethanol gave shiny needles which quickly deteriorated with elimination of HCl and had no sharp melting point. Being aware of this report, we had a closer look at the thermal behavior of **2**. A TGA measurement showed mass losses of 7.1 % at 85 °C. A DSC measurement (heating rate 10 °C/min) in the first heating cycle showed several broad endothermic peaks in this temperature range, which we attribute to the release of residual amounts of ethanol entrapped during crystallization. At 155 °C the DSC measurement showed a single broad peak. Upon heating a sample of **2** at this temperature for several hours, a gas was formed which was chemically identified as HCl. However, the rate of HCl elimation was very small at 160 °C, in agreement with the observation of only a minor mass loss
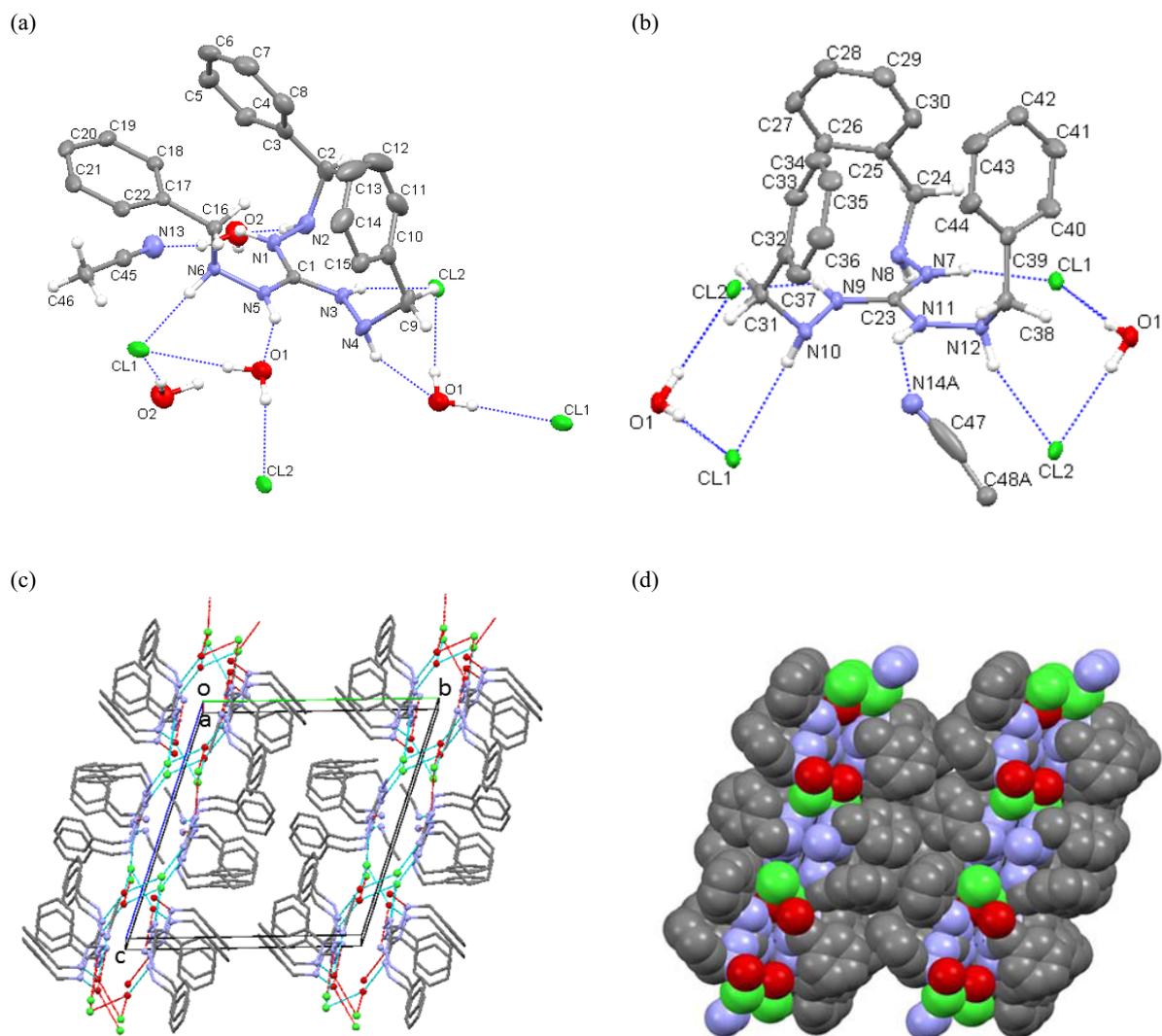

Fig. 1 (color online). Structure of 2 (**3-Cl**) $\times$ 2H$_2$O $\times$ 2CH$_3$CN in the solid state. (a) Cation in conformation A, with hydrogen-bonded Cl$^-$, H$_2$O and CH$_3$CN; hydrogen atoms at phenyl rings are omitted for clarity. (b) The same for cation in conformation B. The acetonitrile molecule is disordered, and only the major position is shown; the unusually large ellipsoid of vibration for C47 is an artefact, as the disorder of this atom could not be resolved computationally. (c) and (d) Wireframe and spacefilling model presentation of the packing and hydrogen bonding network in the solid state, viewed approximately perpendicular to the *b,c* plane (red = O, green = Cl, blue = N, dark gray = C, light grey = H).

in the TGA at this temperature. Thus, we cannot confirm Stollé's observation and conclude that conversion of salt **2** into the neutral guanidine by thermal elimination of HCl is not a practical method.

Solid-state structures

The solid-state structures of salts **3-Cl**, **3-I**, **3-TFA**, and **3-OTf** were determined by single-crystal X-ray diffraction analysis. Molecule plots are shown in Figs. 1 – 4. Selected structural data are given in Table 1. Bond lengths and bond angles in the guanidinium cation are the same in all cases, and the values reflect the complete bond and charge delocalization of the planar CN_3 core. Moreover, all bonding parameters agree well with those of the parent triaminoguanidinium chloride (**1**) [19].

Salt **3-Cl** crystallizes in the triclinic space group $P\bar{1}$ and contains two cations with different conformation, together with two water and two acetonitrile molecules in the asymmetric unit (Figs. 1a and 1b). Conformation A of the cation is an unsymmetrical one, while conformation B is symmetrical with an approximate non-crystallographic C_3 symmetry. The cations of salts **3-I** (Fig. 2a) and **3-TFA** (Fig. 3a) were found to exist in the same unsymmetrical conformation as in **3-Cl** (conformation A). The unsymmetrical conformation A may be described as *exo,endo,endo* and the symmetrical conformation B of **3-Cl** as *endo,endo,endo* with respect to the orientation of the phenyl rings. Salt **3-OTf** exhibits two unsymmetrical conformations of the cation in the solid state, an *exo,endo,endo* (A) and an *exo,exo,endo* (B) conformation (Figs. 4a and 4b). The dihedral angles (Table 1) around the N–N bonds are in the range $116 \pm 15°$ in all cations, and the lone pair of electrons at the outer nitrogen atoms is placed more or less in the CN_3 plane. The dihedral angles around the $N–CH_2$ bond bearing the *exo*-oriented phenyl ring amount to $170.7 – 178.6°$ (*s-trans* conformation). Values of $53.7 – 83.8°$ are found around the $N–CH_2$ bonds bearing the *endo*-oriented phenyl rings, corresponding to a synclinal conformation at these bonds.

The crystal structures of the four salts investigated are coined by the conformation of the cations and by the size and hydrogen bond abilities of the anions. The packing in crystals of **3-Cl** is shown in Figs. 1c and 1d. Cations with conformation A and B are aligned alternatingly in the direction of the crystallographic c axis, with the polar CN_6 platform facing the a,c plane. The

Table 1. Selected bond lengths (Å), angles (deg), and torsion angles (deg) for **3-Cl**, **3-I**, **3-TFA**, and **3-OTf** with estimated standard deviations in parentheses.

|	3-Cl		3-I	3-TFA	3-OTf	
	Conformation A	Conformation B			Conformation A	Conformation B
Distances						
C1–N	1.324(3)–1.332(3)	1.326(3)–1.327(3)	1.321(3)–1.332(3)	1.324(2)–1.333(2)	1.321(3)–1.333(3)	1.321(3)–1.331(2)
N–N	1.408(3)–1.412(2)	1.409(3)–1.412(3)	1.405(2)–1.416(2)	1.405(2)–1.413(2)	1.402(3)–1.410(3)	1.405(3)–1.415(3)
$N–CH_2$	1.461(4)–1.470(4)	1.464(3)–1.470(3)	1.466(3)–1.475(3)	1.464(2)–1.471(2)	1.472(3)–1.476(3)	1.465(4)–1.472(4)
Angles						
$N–C1(C23^a)–N$	119.3(2)–120.7(3)	119.7(2)–120.6(2)	119.6(2)–120.5(2)	119.7(1)–120.3(1)	119.7(2)–120.2(2)	119.7(2)–120.3(2)
$C1(C23^a)–N–N$	116.4(2)–118.5(2)	118.2(2)–118.7(2)	118.3(2)–119.5(2)	117.9(1)–118.9(1)	117.6(2)–118.8(2)	117.2(2)–119.0(2)
$N–N–CH_2$	110.9(2)–112.5(2)	110.9(2)–111.5(2)	110.8(2)–111.8(2)	110.4(1)–110.9(1)	110.3(2)–111.5(2)	111.1(2)–112.2(2)
Torsion angles						
$C1(C23^a)–N–N–CH_2$	−104.7(3), −112.8(2), −101.1(2)	129.6(2), 125.0(2), 126.1(2)	122.8(2), 112.2(2), 131.2(2)	129.1(1), 128.5(1), 114.0(1)	−115.5(2), −134.0(2), −108.4(2)	−124.6(3), −104.4(3), −120.3(3)
$N–N–CH_2–C_{Ph}$	−53.7(3), 68.6(3), 170.7(2)	−79.5(3), −77.1(3), −79.9(3)	175.2(2), −70.6(2), −83.8(2)	−81.2(1), 177.9(1), −72.8(2)	74.4(3), 74.0(3), −178.6(2)	67.6(3), 176.6(2), 176.8(3)

[a] C24 in **3-OTf**.
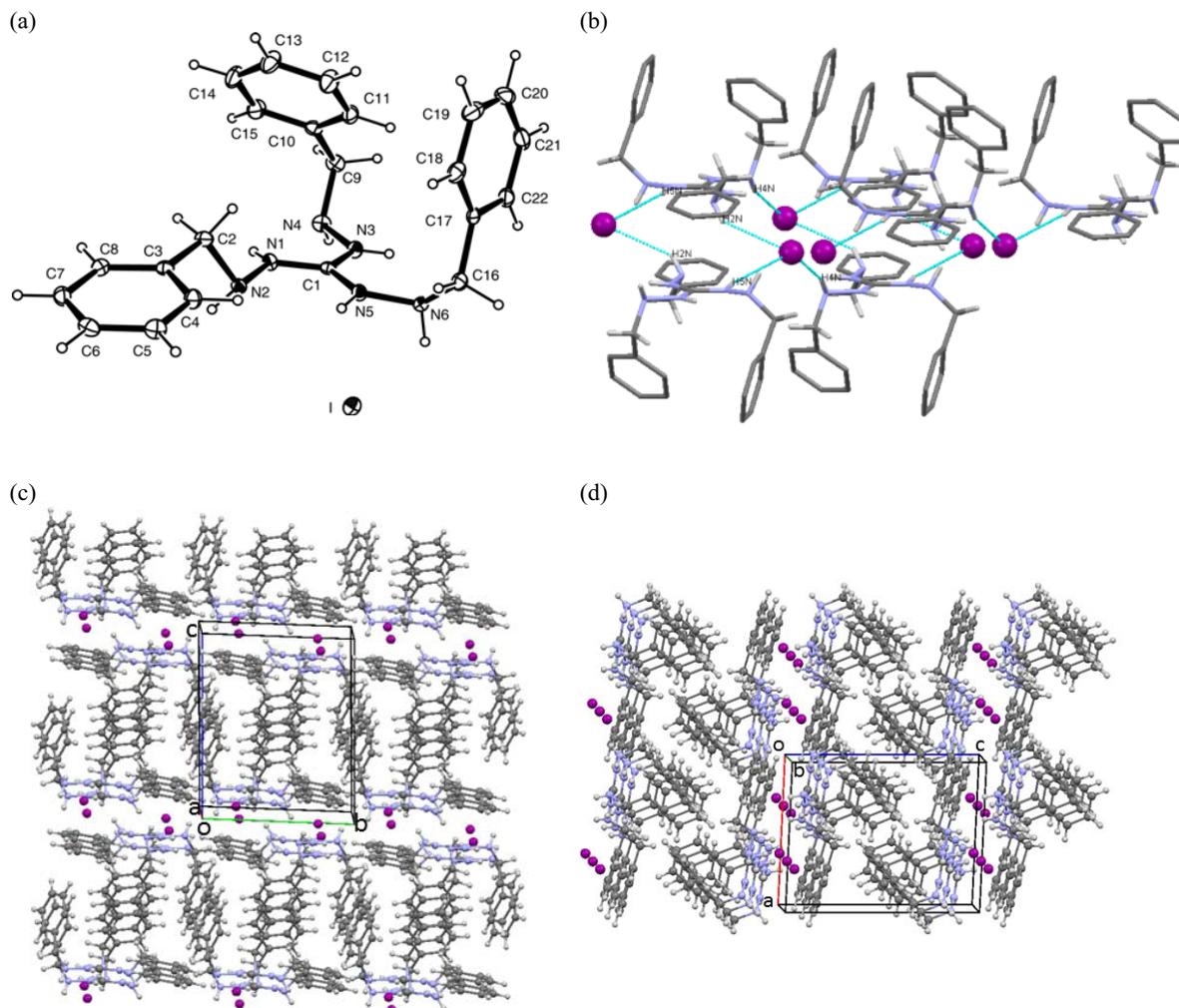
Fig. 2. Structure of salt **3-I** in the solid state. (a) Molecular structure; (b) (color online) short intermolecular contacts involving iodide ions; (c) and (d) (color online) crystal structure viewed approximately perpendicular to the *b,c* and *a,c* plane, respectively (purple = I, blue = N, dark gray = carbon, light grey = H).

benzyl groups are accomodated in the direction of the *b* axis. With the inclusion of cations related by inversion symmetry, the crystal structure consists of an infinite hydrophobic layer, which contains the benzyl groups and has a polar surface on both sides. The space between this polar surface and the adjacent centrosymmetrically related one is filled with chloride ions as well as water and acetonitrile molecules. The repeat distance between the polar layers corresponds to the length of the *b* axis, *i. e.* 16.221 Å. A net of hydrogen bonds connects the cations, the anions, and the solvent molecules (Table 2). For example, cations of

conformation A and B are connected by $C^+N–H\cdots O–H\cdots Cl\cdots H–NC^+$ hydrogen bonds, and the involved chloride ion simultaneously connects the conformation A cation with a centrosymmetrically related one by $Cl\cdots H–O\cdots H–NC^+$ hydrogen bonds.

Compound **3-I** has a similar layer structure in the solid state as described for **3-Cl**, but with a different arrangement and packing of the benzyl rings, which is likely a consequence of the presence of only one conformation of cations (*exo,endo,endo*). The gap between two layers having the polar triaminoguanidinium units at their surfaces is filled with iodide ions which are
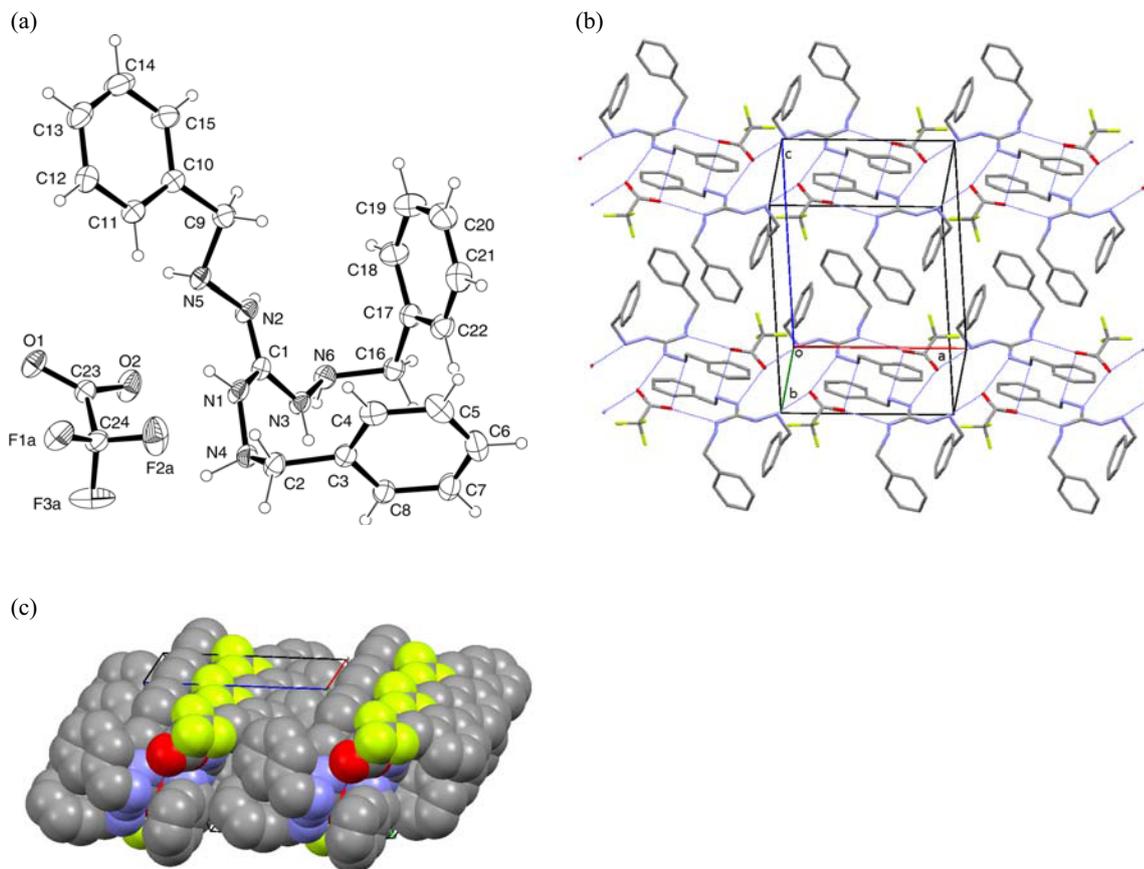
(a)

(b)

(c)

Fig. 3. Structure of salt **3-TFA** in the solid state. (a) Molecular structure; the CF_3 group in the anion is rotationally disordered, only one position is shown. (b) Details of the crystal structure showing with dotted lines the hydrogen bonding pattern; hydrogen atoms themselves have been omitted for clarity. (c) Spacefilling presentation of the molecular packing (color online for (b) and (c); red = O, blue = N, yellow-green = F, dark gray = C).

piled up parallel to the *b* axis (Figs. 2c and 2d); in contrast to **3-Cl**, no solvent molecules are present in this area. The repeat distance between the polar layers is 12.006 Å. Each cation maintains short N–H$\cdots$I contacts to three iodide ions, which in turn connect three cations (Fig. 2b and Table 3). Of the six N–H bonds in a cation, one C^+N–H bond and two C^+NN–H bonds are engaged in hydrogen bonds with I$^-$. Two types of centrosymmetric dimers made up from two cations and two iodide ions can be recognized; hydrogen bonds connect them to form 14- and 16-membered rings (graph sets [20] $R_4^2(14)$ and $R_4^2(16)$), which share a I$\cdots$H–N–NH–C$^+$ bond sequence.

The crystal structure of **3-TFA** is also composed of polar and unpolar layers as described for **3-Cl**,

with a distance of 10.253 Å between the polar layers (Fig. 3c). Two inversion-related rows of cations, which are aligned along the *a* axis, face each other at their polar CN_6 units and are connected by trifluoroacetate ions through N–H$\cdots$O hydrogen bonds (Fig. 3b and Table 3). A cation provides four hydrogen bond donor centers (two C^+N–H, two C^+NN–H), and the trifluoroacetate anion accepts two hydrogen bonds at each oxygen atom, thereby connecting three cations with each other. The carboxylate group of the anion coordinates with a NH–NH unit of the cation to form a seven-membered ring motif (graph set $R_2^2(7)$); in addition, one oxygen atom connects with C^+N–H of a centrosymmetrically related cation, and the other oxygen atom connects with C^+NN–H of the adjacent
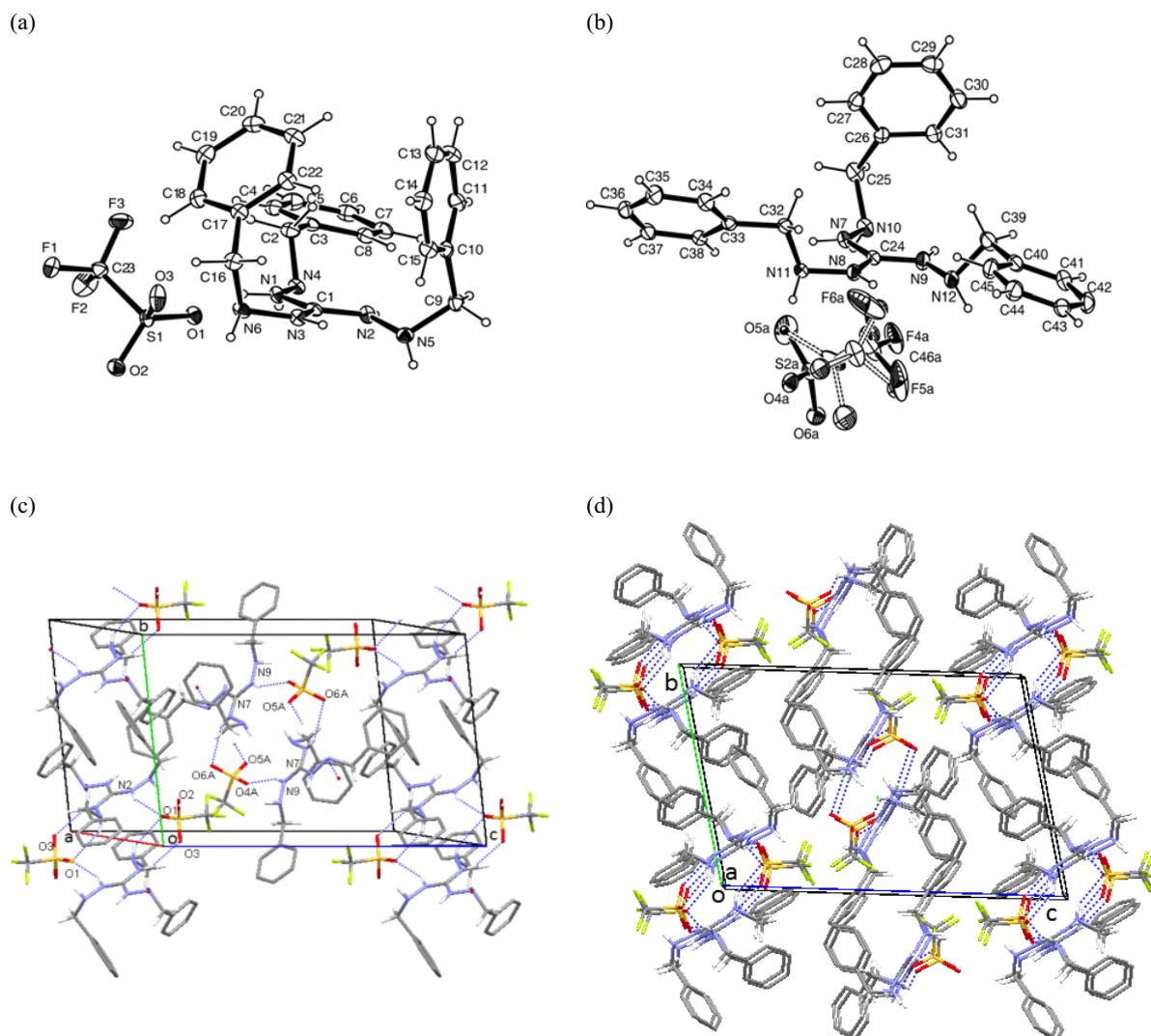
(a)

(b)

(c)

(d)

Fig. 4. Structure of salt **3-OTf** in the solid state. (a) Molecular structure of the ion pair with cation in conformation A (*exo*, *endo*, *endo*). (b) Molecular structure of the ion pair with cation in conformation B (*exo*, *exo*, *endo*); the triflate anion is disordered, the minor species is shown with dashed bonds. (c) Details of the hydrogen bonding pattern; H atoms on phenyl rings are omitted for clarity (color online; red = O, blue = N, orange = S, yellow-green = F, dark gray = C, light grey = H). (d) Packing motifs, viewed almost perpendicular to the *b*,*c* plane (color online).

cation, thus becoming part of a centrosymmetric 14-membered ring motif ($R_4^2(14)$).

In the crystal structure of **3-OTf**, conformation A and B cations are involved in separate centrosymmetric dimers made up from two cations and two triflate anions and held together by N–H···O hydrogen bonds (Fig. 4c). Conformation A cations provide four N–H donors (two C^+N–H and two C^+NHN–H), and

all three oxygen atoms of the associated triflate are involved in hydrogen bonding. A C^+–NH–NH unit of the cation coordinates *via* H bonds with a O–S–O unit of the anion, thus forming a $R_2^2(7)$ motif, and one of these oxygen atoms additionally connects to C^+N–H of a centrosymmetrically related cation. Insofar, the coordination motif in the centrosymmetric dimer is the same as for **3-TFA**. Coordination to a third cation by

Table 2. Intermolecular hydrogen bonds in the solid-state structure of **3-Cl** (2 **3-Cl**, 2 CH_3CN, 2 H_2O)[a].

Donor–H···Acceptor (D–H···A)	d(D–H) (Å)	d(H···A) (Å)	d(D–A) (Å)	Angle DHA (deg)
N2–H2N···O2	0.95	1.92	2.865	174.3
N3–H3···Cl2[b]	0.90	2.36	3.201	155.2
N4–H4N···O1[b]	0.89	2.39	3.206	152.6
N5–H5N···O1[c]	0.90	2.21	3.031	151.1
N6–H6N···Cl1	0.90	2.58	3.394	151.5
N7–H7N···Cl1[d]	0.90	2.55	3.260	135.9
N9–H9···Cl2[e]	0.90	2.47	3.244	143.8
N10–H10N···Cl1[f]	0.88	2.57	3.372	150.9
N11–H11N···N14A	0.90	2.22	2.934	136.5
N12–H12N···Cl2	0.93	2.44	3.330	159.9
O1–H101···Cl2	0.86	2.37	3.217	170.3
O1–H201···Cl1[d]	0.86	2.31	3.167	175.2
O2–H102···Cl1	1.08	2.05	3.100	164.4
O2–H202···N13[b]	1.03	1.97	2.894	148.0
C46–H46A···Cl2[g]	0.98	2.78	3.744	167.0

[a] See Figs. 1a and b for atom numbering; estimated standard deviations are ± 0.02 Å for N–H and H···A bonds, $\pm 0.002 - 0.003$ Å for D···A distances, and $\pm 2°$ for D–H···A angles. Symmetry codes: [b] $-x+1, -y, -z$; [c] $x+1, y, z$; [d] $x-1, y, z$; [e] $-x, -y, -z+1$; [f] $-x+1, -y, -z+1$; [g] $x, y-1, z$.

an O···H–NNHC[+] bond is mediated, however, by the third sulfonate oxygen, while in **3-TFA** this role is played by the second carboxylate oxygen atom which maintains two O···H–N bonds. The hydrogen bonding pattern in the centrosymmetric dimer containing

conformation B cations is simpler. The cation is engaged in only three N–H···O bonds, while each sulfonate oxygen atom connects to a different cation. The H–N–C[+]–N–H moiety of two cations and the O–S–O unit of two anions form a 16-membered ring ($R_4^4(16)$), and the third sulfonate oxygen atom is associated with C[+]NHN–H of a third cation. Table 3 also lists the two shortest N–H···F contacts (2.41, 2.50 Å), indicating that the fluorine atoms of the triflate anions have no intermolecular contacts shorter than the sum of van der Waals radii.

The molecular packing in the crystal of **3-OTf** (Fig. 4d) can be described by two arrangements. Firstly, the layered structure described for the other salts can be recognized again. In the projection shown, the layers are oriented diagonally (repeat distance 11.700 Å), the polar layer is bisected by the (111) plane, and a sequence of alternating centrosymmetric dimers (as described above) with conformation A and B cations is seen. In contrast to the packing in **3-Cl**, only the CN_3 plane of the cation with conformation A is almost parallel to the (111) plane, while the planar CN_3 core of the more extended conformation B cation is significantly tilted against this plane. Secondly, the two types of centrosymmetric dimers are found in separate layers parallel to the *b* axis, and they are not connected by hydrogen bonds.

Table 3. Intermolecular hydrogen bonds and short contacts in the solid-state structures of salts **3-I, 3-TFA**, and **3-OTf**[a].

Compound	Donor–H···Acceptor (D–H···A)	d(D–H) (Å)	d(H···A) (Å)	d(D–A) (Å)	Angle DHA (deg)	Symmetry code (A)
3-I	N2–H2N···I	0.88(2)	2.94(2)	3.648(2)	138.7(17)	$-x+1, -y+1, -z+2$
	N4–H4N···I	0.89(2)	2.81(2)	3.669(2)	161.8(19)	$x+1, y, z$
	N5–H5N···I	0.87(2)	2.91(2)	3.635(2)	142.7(19)	
3-TFA	N1–H1N···O2	0.88(2)	2.09(2)	2.815(2)	139.6(15)	
	N2–H2N···O1	0.90(2)	2.08(2)	2.874(2)	146.1(16)	$-x+1, -y+1, -z$
	N5–H5N···O2	0.91(2)	2.22(2)	3.034(2)	149.2(15)	$-x+1, -y+1, -z$
	N6–H6N···O1	0.91(2)	2.12(2)	2.997(2)	162.4(15)	$x–1, y, z$
3-OTf	N1–H1N···O3	0.90(2)	2.18(2)	2.953(3)	144(2)	
	N2–H2N···O1	0.89(2)	2.06(2)	2.824(2)	143(3)	$-x+1, -y, -z$
	N4–H4N···O1	0.90(2)	2.27(2)	3.036(3)	143(2)	
	N4–H4N···N4	0.90(2)	2.53(3)	3.084(4)	120(2)	$-x+1, -y, -z$
	N6–H6N···O2	0.91(2)	2.10(2)	2.950(3)	156(2)	$-x, -y, -z$
	N7–H7N···O6A	0.90(2)	2.29(3)	3.002(4)	135(3)	$-x+2, -y+1, -z+1$
	N8–H8N···F4A	0.92(2)	2.36(3)	3.210(4)	155(3)	
	N9–H9N···O4A	0.92(2)	2.16(4)	2.963(3)	145(3)	$x+1, y, z$
	N10–H10N···N10	0.85(2)	2.50(3)	3.048(5)	122(3)	$-x+3, -y+1, -z+1$
	N11–H11N···O5A	0.92(2)	2.26(2)	3.023(7)	140(2)	
	N12–H12N···F1	0.92(4)	2.46(2)	3.345(3)	162(4)	$x+1, y, z$

[a] See Figs. 2a, 3a, 4a, and 4b for atom numbering; estimated standard deviations are given in parentheses.

Table 4. Crystallographic data for triaminoguanidinium salts **3-Cl**, **3-I**, **3-TFA**, and **3-OTf**.

	3-Cl	3-I	3-TFA	3-OTf
Formula	$C_{22}H_{27}ClN_6 \times$ $CH_3CN \times H_2O$	$C_{22}H_{27}IN_6$	$C_{24}H_{27}F_3N_6O_2$	$C_{23}H_{27}F_3N_6O_3S$
M_r	470.02	502.40	488.52	524.57
Crystal size, mm^3	$0.32 \times 0.23 \times 0.11$	$0.22 \times 0.21 \times 0.20$	$0.22 \times 0.17 \times 0.11$	$0.25 \times 0.18 \times 0.05$
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.5273(4)	9.8029(3)	10.2525(5)	10.4611(4)
b, Å	16.2206(6)	10.0279(3)	11.1791(7)	12.9343(9)
c, Å	16.6439(5)	12.0055(4)	12.4033(6)	19.7693(14)
α, deg	104.944(3)	90.704(3)	116.412(6)	101.123(6)
β, deg	94.353(3)	91.522(3)	92.842(4)	100.514(5)
γ, deg	108.190(3)	105.225(3)	101.564(5)	97.482(5)
V, Å^3	2570.58(16)	1138.12(6)	1231.67(12)	2542.4(3)
Z	4	2	2	4
D_{calcd}, g cm^{-3}	1.21	1.47	1.32	1.37
μ, mm^{-1}	1.6	1.4	0.9	1.7
$F(000)$, e	1000	508	512	1096
Radiation	CuK_α	MoK_α	CuK_α	CuK_α
Temperature, K	193(2)	190(2)	190(2)	193(2)
hkl range	$\pm13, \pm20, \pm20$	$\pm12, \pm12, \pm15$	$-12 \to 11, \pm13, -11 \to 15$	$\pm12, -10 \to 15, \pm23$
θ range, deg	3.00 – 74.58	2.73 – 27.10	4.03 – 74.15	4.49 – 66.60
Refl. measured / unique	43837 / 10281	18645 / 5006	8866 / 4827	16752 / 8987
R_{int}	0.0344	0.0353	0.0165	0.0309
Param. refined / restraints	620 / 6	286 / 6	353 / 6	740 / 27
$R(F)/wR(F^2)^{a, b}$ [$I > 2\sigma(I)$]	0.0553/0.1507	0.0240/0.0500	0.0419/0.1096	0.0494/0.1340
$R(F)/wR(F^2)^{a, b}$ (all refl.)	0.0704/0.1601	0.0288/0.0526	0.0481/0.1168	0.0603/0.1534
GoF $(F^2)^c$	1.115	1.033	0.969	1.110
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.72 / −0.66	0.32 / −0.38	0.29 / −0.33	0.65 / −0.51
CCDC number	874410	874411	874412	874413

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Conclusion

1,2,3-Tris(benzylamino)guanidinium chloride (**3-Cl**) can be prepared readily from triaminoguanidinium chloride and benzaldehyde by reductive benzylation of the three NH_2 groups. Other salts **3-X** are easily obtained by anion exchange reactions. The cation of **3-X** salts has a time-averaged threefold symmetry in solution according to the ^{1}H and ^{13}C NMR spectra, but several conformations are present in the solid state of the four salts (X = Cl, I, O_2CCF_3, OTf) investigated. While the three benzyl groups are positioned on the same face of the almost planar $C(NN)_3$ core of the cation, rotation around the (N)N–C(Ph) single bond gives rise to conformations with different orientations of the phenyl rings. The conformations found were as follows: *exo,endo,endo* as well as *endo,endo,endo* in **3-Cl**, *exo,endo,endo* in **3-I** and 3-O_2CCF_3, *exo,endo,endo* as well as *exo,exo,endo* in **3-OTf**. The variation of the anion has an impact not only on the conformation(s) of the cation, but also on the crystal structure, depending not only on the size and shape of the anion but also on the geometry of the hydrogen bonding pattern connecting cations and anions. Of particular interest in terms of crystal engineering might be the crystal structures of **3-Cl** and **3-I** which are made up from stacked bilayers containing unpolar benzyl rings in the interior and the polar guanidinium cores at both faces, with the guanidinium groups embracing infinite channels which are filled with the anions and eventually solvent molecules.

Experimental Section

General information

NMR spectra were recorded using a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{19}F: 376.47 MHz, ^{11}B: 128.38 MHz). ^{1}H and ^{13}C NMR

spectra were referenced to the residual proton signal of the solvent; ^{1}H: δ(CHCl$_3$) = 7.26, δ((CH$_3$)$_2$SO) = 2.50, δ(CO(CH$_3$)$_2$) = 2.05 ppm; ^{13}C: δ(CDCl$_3$) = 77.0, δ((CD$_3$)$_2$SO) = 39.43, δ(CO(CD$_3$)$_2$) = 30.83 ppm. ^{19}F spectra were referenced to external C$_6$F$_6$, ^{11}B spectra to external BF$_3$ etherate. IR spectra were recorded on KBr pellets with a Bruker Vector 22 FTIR instrument. Elemental analyses were made with an elementar Hanau vario MICRO cube analyzer. Melting points were determined with a Büchi B-540 instrument at a heating rate of 3 °C min^{-1}. Thermogravimetric analysis: Mettler-Toledo TGA/SDTA 851 instrument, heating range 25 – 1100 °C, rate 10 °C min^{-1}, 50 mL min^{-1} N$_2$. DSC: Differential scanning calorimetry (DSC): Perkin Elmer DSC 7 calorimeter.

N,N′,N″-Tris(benzyliminyl)guanidinium chloride (2)

N,N′,N″-Triaminoguanidinium chloride [1] (**1**, 5.15 g, 36.6 mmol) was dissolved in 35 mL of water and 70 mL of ethanol at 80 °C. A solution of benzaldehyde (12.72 g, 120 mmol) in ethanol (50 mL) was gradually added from an addition funnel, and the mixture was subsequently heated at reflux for 1 h. The yellow solution was cooled at ambient temperature, then kept at −32 °C for 48 h for crystallization. The deposited crystals were collected, and further batches were obtained from the mother liquor in additional crystallization steps. Salt **2** was obtained as pale-yellow fine needles in a combined yield of 14.65 g (36.2 mmol, 98.9 %), m. p. 185 °C (dec.). – IR (KBr): ν = 3420 (br, m, N–H), 3028 (m), 1635 (s, N=C), 1450 (m), 1311 (m), 1226 (m), 1097 (m), 1072 (m), 757 (m), 692 (m) cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.53 – 7.51 (m, 9 H, Ar-H), 8.05 – 8.03 (m, 6 H, Ar-H), 8.93 (s, 3 H, N=CH), 12.38 (s, 3 H, C$^+$–NH) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 128.20 (*o*-C$_{Ph}$), 128.71 (*m*-C$_{Ph}$), 130.99 (*p*-C$_{Ph}$), 133.04 (*i*-C$_{Ph}$), 148.97 (C$^+$N$_3$), 151.22 (Ph*C*H=N) ppm. – C$_{22}$H$_{21}$N$_6$Cl (404.9): calcd. C 65.26, H 5.23, N 20.76; found C 65.17, H 5.29, N 20.52.

N,N′,N″-Tris(benzylamino)guanidinium chloride (3-Cl)

Salt **2** (5.00 g, 12.2 mmol) was dissolved in methanol (180 mL), Pd/C (10 %) (259 mg, 243 μmol) was added, and the mixture was kept stirring for 14 h under an atmosphere of hydrogen. The catalyst was removed by filtration through a glass frit (pore size 10 – 16 μm) and the solvent was distilled off, last traces being removed at 0.05 mbar. Recrystallization from acetonitrile (40 mL) yielded salt **3-Cl** as colorless fine needles (3.91 g, 9.5 mmol, 78 %), m. p. 143 – 144 °C. – IR (KBr): ν = 3415 (br, m), 3342 (m), 3200 (br, s, N–H), 3063 (w), 3033 (w), 2976 (s), 1653 (s, N=C), 1496 (m), 1454 (m), 901 (m), 753 (s), 735 (s), 702 (s) cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 3.71 (s, 6 H, NHC*H*$_2$), 5.46 (s,

3 H, NH), 7.30 – 7.31 (m, 15 H, Ar-H), 8.72 (s, 3 H, C$^+$NH) ppm. – ^{1}H NMR (CDCl$_3$): δ = 3.59 (s, 6 H, NHC*H*$_2$), 5.02 (s, 3 H, NH), 7.09 – 7.11 (m, 6 H, H$_{Ph}$), 7.15 – 7.20 (m, 9 H, H$_{Ph}$), 7.99 (s, 3 H, C$^+$NH) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 54.27 (Ph*C*H$_2$), 127.19 (*p*-C$_{Ph}$), 128.02 (*o*-C$_{Ph}$), 128.88 (*m*-C$_{Ph}$), 136.82 (*i*-C$_{Ph}$), 156.84 (C$^+$N$_3$) ppm. – C$_{22}$H$_{27}$N$_6$Cl (404.90): calcd. C 64.30, H 6.62, N 20.45; found C 64.35, H 6.53, N 20.25.

N,N′,N″-Tris(benzylamino)guanidinium iodide (3-I)

Salt **3-Cl** (820 mg, 2.0 mmol) was dissolved in acetonitrile (40 mL), and methyl iodide (374 μL, 6.0 mmol) was added. The mixture was kept boiling for 20 h, resulting in a yellow solution. The solvent was evaporated, and the solid residue was washed with acetonitrile and then dried at 0.05 mbar. Salt **3-I** was left as a colorless solid (760 mg, 1.51 mmol, 76 %). – M. p. 173 °C. – IR (KBr): ν = 3338 (br, s, N–H), 3211 (br, s, N–H), 3062 (w), 3030 (w), 1650 (s, N=C), 1452 (m), 930 (m), 897 (m), 761 (s), 747 (s), 700 (s) cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 3.70 (s, 6 H, PhC*H*$_2$N), 5.37 (s, 3 H, NH), 7.25 – 7.32 (m, 15 H, H$_{Ph}$), 8.68 (s, 3 H, C$^+$NH) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 54.11 (Ph*C*H$_2$N), 127.08 (*p*-C$_{Ph}$), 127.91 (*o*-C$_{Ph}$), 128.77 (*m*-C$_{Ph}$), 136.62 (*i*-C$_{Ph}$), 156.67 (C$^+$N$_3$) ppm. – C$_{22}$H$_{27}$N$_6$I (502.39): calcd. C 52.60, H 5.42, N 16.73; found C 52.52, H 5.46, N 16.61.

N,N′,N″-Tris(benzylamino)guanidinium trifluoroacetate (3-TFA)

In a reaction flask protected from light with aluminum foil, salt **3-Cl** (410 mg, 1.00 mmol) was dissolved in chloroform (10 mL), and solid silver(I) trifluoroacetate (230 mg, 1.05 mmol) was added. The mixture was kept stirring for 15 h, and the precipitate was removed by centrifugation. The filtered solution was evaporated to dryness; last traces of solvent were removed at 0.05 mbar. Salt **3-TFA** was left as a colorless solid (480 mg, 0.98 mmol, 98 %). – M. p. 129 °C. – IR (KBr): ν = 3361 (m), 3264 (br, s, N–H), 3033 (m), 1639 (br, s, C=O), 1494 (m), 1454 (m), 1419 (m), 1368 (m), 1317 (m), 1192 (s, C–F), 1143 (s, C–F), 998 (m), 962 (m), 922 (m), 827 (m), 800 (m), 748 (s), 699 (s) cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 3.71 (d, ^3J = 5.2 Hz, 6 H, C*H*$_2$NH), 5.44 (t, ^3J = 5.2 Hz, 3 H, CH$_2$N*H*), 7.29 – 7.35 (m, 15 H, H$_{Ph}$), 8.75 (s, 3 H, C$^+$NH) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 54.57 (Ph*C*H$_2$NH), 117.50 (q, $^1J_{C,F}$ = 299.9 Hz, *C*F$_3$COO$^-$), 127.40 (*p*-C$_{Ph}$), 128.20 (*m*-C$_{Ph}$), 129.10 (*o*-C$_{Ph}$), 137.00 (*i*-C$_{Ph}$), 157.00 (C$^+$N$_3$), 158.40 (q, $^1J_{C,F}$ = 30.8 Hz, CF$_3$*C*OO$^-$) ppm. – ^{19}F NMR ([D$_6$]DMSO): δ = −73.07 ppm. – C$_{24}$H$_{27}$F$_3$N$_6$O$_2$ (488.21): calcd. C 59.01, H 5.57, N 17.20; found C 59.07, H 5.80, N 17.38.

N,N′,N″-Tris(benzylamino)guanidinium tetrafluoroborate (3-BF₄)

In a reaction flask protected from light with aluminum foil, salt **3-Cl** (205 mg, 0.5 mmol) was dissolved in dichloromethane (10 mL), and solid silver(I) tetrafluoroborate (97 mg, 0.5 mmol) was added. The mixture was kept stirring for 20 h, and the precipitate was removed by filtration. The filtered solution was evaporated to dryness, last traces of solvent being removed at 0.05 mbar. Salt **3-BF₄** was left as a colorless solid (190 mg, 0.41 mmol, 82 %). – M. p. 145 °C. – IR (KBr): $v = 3337$ (s), 3064 (w), 3032 (w), 1657 (s), 1453 (m), 1368 (m), 1060 (br, s, BF_4^-), 748 (m, BF_4^-), 700 (m) cm^{-1}. – ^{1}H NMR ([D₆]DMSO): $\delta = 3.71$ (s, 3 H, CH_AH$_B$NH), 3.72 (s, 3 H, CH$_A$H$_B$NH), 5.41 (s, 3 H, CH$_2$NH), 7.25 – 7.35 (m, 15 H, H$_{Ph}$), 8.72 (s, 3 H, C$^+$-NH) ppm. – ^{13}C NMR ([D₆]DMSO): $\delta = 54.40$ (PhCH$_2$NH), 127.30 (p-C$_{Ph}$), 128.20 (m-C$_{Ph}$), 129.10 (o-C$_{Ph}$), 136.90 (i-C$_{Ph}$), 157.00 (C$^+$N$_3$) ppm. – ^{19}F NMR ([D₆]DMSO): $\delta = -147.84$ ppm. – ^{11}B NMR ([D₆]DMSO): $\delta = -0.56$ ppm. – C$_{22}$H$_{27}$BF$_6$N$_6$ (462.23): calcd. C 57.16, H 5.89, N 18.18; found C 57.50, H 6.24, N 18.43.

N,N′,N″-Tris(benzylamino)guanidinium trifluoromethanesulfonate (3-OTf)

Salt **3-Cl** (410 mg, 1.0 mmol) was dissolved in chloroform (10 mL), and solid silver(I) trifluoromethanesulfonate (260 mg, 1.0 mmol) was added. Precipitation of AgCl started within 5 min. The mixture was kept stirring for 16 h, then the precipitate was separated by filtration or centrifugation. The solvent was evaporated, last traces being removed at 0.05 mbar. Salt **3-OTf** was left as a yellowish solid (511 mg, 0.97 mmol, 97 %). – M. p. 109 °C. – IR (KBr): $v = 3304$ (br, s, N–H), 3066 (m), 3033 (m), 1653 (s, N=C), 1498 (m), 1455 (m), 1225 (s, sulfonate), 1172 (s, CF$_3$), 1026 (s, sulfonate), 982 (m), 876 (m), 792 (m), 749 (s), 699 (s) cm^{-1}. – ^{1}H NMR ([D₆]acetone): $\delta = 3.86$ (d, $^3J = 5.3$ Hz, 6 H, CH_2NH), 5.09 (t, $^3J = 5.3$ Hz, 3 H, CH$_2$NH), 7.29 – 7.35 (m, 15 H, H$_{Ph}$), 8.52 (s, 3 H, C$^+$NH) ppm. – ^{13}C NMR (CDCl$_3$): $\delta = 55.50$ (PhCH$_2$N), 120.34 (q, $^1J_{C,F} = 319.0$ Hz, CF$_3$SO$_3^-$), 127.69 (p-C$_{Ph}$), 128.35 (o-C$_{Ph}$), 129.71 (m-C$_{Ph}$), 136.18 (i-C$_{Ph}$), 156.17 (C$^+$N$_3$) ppm. – ^{19}F NMR ([D₆]DMSO): $\delta = -77.43$ ppm. – C$_{22}$H$_{27}$F$_3$N$_6$O$_3$S (524.56): calcd. C 52.66, H 5.19, N 16.02; found C 52.45, H 5.24, N 15.80.

X-Ray structure determinations

Crystallization of **3-Cl** by the diffusion method using acetonitrile/pentane gave clear prismatic crystals of **3-Cl** × H$_2$O × CH$_3$CN, which after isolation became turbid within minutes due to the loss of solvate molecules and had to be handled accordingly for the data collection. Suitable crystals of **3-I** and **3-OTf** were grown from acetonitrile and ethanol, respectively, by slow evaporation of the solvent, those of **3-TFA** by the diffusion method using acetone/pentane. Low-temperature data collection was carried out on an XcaliburS diffractometer (Oxford Diffraction). The structures were solved by Direct Methods and refined on F^2 values using a full-matrix least-squares method. For salt **3-Cl**, hydrogen atom positions at the "inner" nitrogen atoms of the cation were calculated geometrically (d(N–H) = 0.90 Å) and treated by the riding model in the refinement procedure; all other hydrogen atom positions were located in a difference electron density map and refined freely. For the other salts, the NH hydrogen atom positions were taken from a ΔF map and included in the refinement with the DFIX keyword (d(N–H) target values taken from the interpretation of the ΔF map), all other hydrogen atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. In the crystal structure of **3-Cl**, one acetonitrile molecule is disordered and the hydrogen atom positions were not localized; the major position could be refined reasonably, while a second molecule, disordered mainly by rotation (in-plane and probably out-of-plane) around an axis perpendicular to the axis of the first molecule, was included in the refinement, too, but gave no reasonable bond geometries. In the crystal structure of **3-TFA**, the CF$_3$ group is rotationally disordered. Two sets of positions for the F atoms could be refined. In the crystal structure of **3-OTf**, which contains two cation/anion pairs in the asymmetric unit, one CF$_3$SO$_3$ anion is disordered over two positions with refined occupancy factors of 0.81 and 0.19. Despite the introduction of restraints, the positions of the minor component could not be refined satisfactorily for all atoms.

Software for structure solution and refinement: SHELXL-97 [21]; molecule plots: ORTEP-3 [22] and MERCURY [23]. Further details are provided in Table 4.

CCDC 874410–874413 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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