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Guanidinium Alkynesulfonates with Single-Layer Stacking Motif: Interlayer Hydrogen Bonding Between Sulfonate Anions Changes the Orientation of the Organosulfonate R Group from "Alternate Side" to "Same Side"

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Abstract: Hydrolyses of $HC{\equiv}CSO_3SiMe_3$ (**1**) and $CH_3C{\equiv}CSO_3SiMe_3$ (**2**) lead to the formation of acetylenic sulfonic acids $HC{\equiv}CSO_3H{\cdot}2.33\,H_2O$ (**3**) and $CH_3C{\equiv}CSO_3H{\cdot}1.88\,H_2O$ (**4**). These acids were reacted with guanidinium carbonate to yield $[^+C(NH_2)_3][HC{\equiv}CSO_3^-]$ (**5**) and $[^+C(NH_2)_3][CH_3C{\equiv}CSO_3^-]$ (**6**). Compounds **1**–**6** were characterized by spectroscopic methods, and the X-ray crystal structures of the guanidinium salts were determined. The X-ray results of **5** show that the guanidinium cations and organosulfonate anions associate into 1D ribbons through $R_2^2(8)$ dimer interactions, whereas association of these ions in **6** is achieved through $R_2^2(8)$ and $R_2^1(6)$ interactions. The ribbons in **5** associate into 2D sheets through $R_2^2(8)$ dimer interactions and $R_6^3(12)$ rings, whereas those in **6** are connected through $R_2^1(6)$ and $R_2^2(8)$ dimer interactions and $R_6^4(14)$ rings. Compound **6** exhibits a single-layer stacking motif similar to that found in guanidinium alkane- and arenesulfonates, that is, the alkynyl groups alternate orientation from one ribbon to the next. The stacking motif in **5** is also single-layer, but due to interlayer hydrogen bonding between sulfonate anions, the alkynyl groups of each sheet all point to the same side of the sheet.

Keywords: alkynes · crystal engineering · guanidinium sulfonate · hydrogen bonds · sulfonation

Introduction

Hydrogen bonding is nature's favourite way of keeping molecules tightly bound to one another. This is presumably because most organic compounds have sites that are capable of hydrogen bonding, ranging from weakly polarized C–H bonds to strongly polarized OH groups. Its strength depends on the nature of the atoms involved in the A–H···B connection and, because it is a directional interaction, it is also contingent on the distance between the H and B centers and on the A-H-B angle.[1–5]

Due to its great versatility, hydrogen bonding has become a key interaction in crystal engineering.[6–8] Numerous modules possessing hydrogen-bonding capabilities have been described in the literature and used to construct supramolecular assemblies. Guanidinium organosulfonates, $C(NH_2)_3^+$ RSO_3^-, in which RSO_3^- may be an alkane- or an arenesulfonate anion, belong to this category.[9–19]

Guanidinium sulfonates form robust hydrogen-bonded networks. It was suggested that this is due to a combination of several factors: the large number of strong hydrogen bonds, the matched number of donors and acceptors (six guanidinium protons and six electron pairs on the three sulfonate oxygen atoms), threefold topologies for both the guanidinium and RSO_3^- ions, similar sizes of the two partners, and the presence of Coulombic interactions between the oppositely charged ions.[10,12,13] In the solid state, guanidinium cations and organosulfonate anions are tightly bonded through $R_2^2(8)$ dimer interactions.[20] Repetition of this associative sequence along an axis results in the formation of infinite ribbons (Scheme 1). Association of these 1D ribbons through $R_2^2(8)$ dimer interactions and $R_6^3(12)$ rings in a direc-

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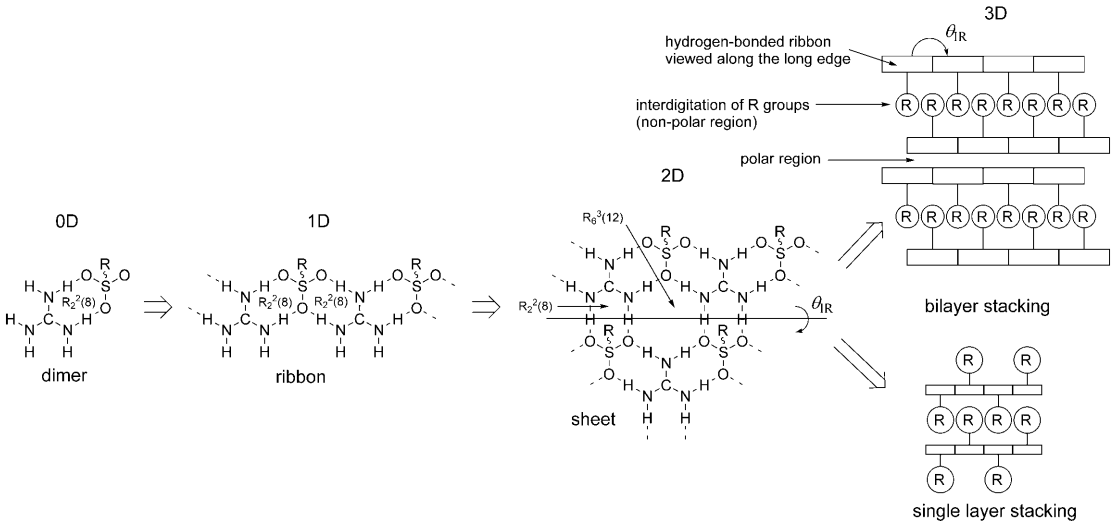


Scheme 1. Schematic representation showing the arrangement of the guanidinium sulfonate motif as a function of increasing dimension.

tion perpendicular to the first one generates 2D sheets made of quasi-hexagonal patterns. This "honeycomb" structure appears to be general and has been observed for most guanidinium monosulfonates.

The "honeycomb" structure is not perfectly flat, but is puckered. The degree of puckering, as measured by the θ_{IR} angle made by two adjacent ribbons (Scheme 1), is a function of the size of the R group of the sulfonate anion. For small R groups, corrugation is not severe and θ_{IR} is close to 180°. In this case, all of the R groups within a sheet are oriented to the same side of the sheet. For bulky R groups, θ_{IR} may be as low as 77°.[12] In this case, R groups within a sheet are not oriented to the same side of the sheet, but rather they alternate orientation from one ribbon to the next. Thus, the hydrogen-bonded sheet structure is preserved no matter what the size of the RSO_3^- ion; this demonstrates the adaptability of the guanidinium sulfonate network.

The 2D sheets pile up in the third dimension according to two different motifs (Scheme 1).[9,11–13] If the alkane or arene groups of the sulfonate anions are small, interdigitation of these groups is possible in the nonpolar region separating the sheets; this results in a bilayer stacking of the sheets. If the RSO_3^- ions are sterically demanding, interdigitation of the R groups is not possible, and this results in the formation of single-layer motifs.

Structural studies have been carried out on guanidinium arenesulfonates bearing substituents capable of hydrogen bonding.[10,13] These substituents were found to interfere with the guanidinium sulfonate hydrogen-bond network, which leads to severe perturbation and, in some cases, disruption of the quasi-hexagonal structure. The degree of perturbation decreased in the order $COOH > OH > NO_2$, in agreement with the ability of these groups to form strong hydrogen bonds.

Another intriguing feature of guanidinium arenesulfonates is their ability to form inclusion compounds when crystallized from certain aromatic solvents.[14,16,19] The bilayer stacking motif observed in guest-free compounds is not encountered in host–guest complexes, presumably because interdigitation of the organosulfonate R groups in the nonpolar region separating the sheets precludes the inclusion of solvent molecules. On the other hand, a single-layer structure is observed in which the solvent molecules are interdigitated with the R groups of the RSO_3^- ions. Compounds that crystallize with this type of architecture have been termed "continuously layered inclusion compounds" abbreviated CLIC. In these CLICs, the number of guest molecules per guanidinium sulfonate unit is one. Another structural arrangement exists that is found in "tubular inclusion compounds" abbreviated TIC. These TICs consist of six-sided discrete tubes, each comprising six guanidinium sulfonate ribbons. The tubes assemble into a hexagonal array with the R groups of the RSO_3^- ions directed towards the outside of the tubes. There are two thirds of a guest per guanidinium sulfonate unit: one third of a guest occupies the interior of the tubes and the remaining third is located in the region between the tubes.

The thermal behavior of guanidinium alkylbenzenesulfonates and guanidinium alkylbiphenylsulfonates has been investigated by using various techniques including polarizing optical microscopy, differential scanning calorimetry, dilatometry, infrared spectroscopy, and X-ray diffraction.[21,22] These compounds turn into persistent smectic liquid-crystal phases upon heating, and this phenomenon was ascribed to the reinforcement provided by the hydrogen-bonded network. Furthermore, rheology studies indicated the persistence of intermolecular hydrogen bonding in the liquid-crystalline state.[22] Interestingly, unlike sodium alkylbenzenesulfonates, guanidinium alkylbenzenesulfonates also exhibit lyotropic behavior in aqueous and organic solvents, and this discrepancy was attributed to the fact that hydrogen bonding mediated by the guanidinium ion was required for gel formation.[23] Recently, smectic liquid-crystalline phases were reported for guanidinium alkanesulfonates.[24]

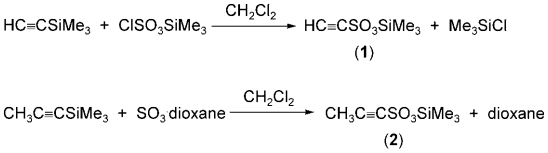
Ward and co-workers also prepared and characterized crystallographically a series of guanidinium α,ω-alkane- and arenedisulfonates and showed that these compounds crystallized with pillared architectures.[25–35] The disulfonate pillars connect opposing hydrogen-bonded sheets, resulting in the formation of cavities between the sheets. When long enough pillars are used, the cavities are sufficiently large to accommodate solvent molecules. In this respect, guanidinium organodisulfonates have been regarded as functional organic zeolite analogues.[36] These clathrates exhibit various kinds of architectures (discrete bilayer, simple brick, crisscross bilayer, double brick, zigzag brick, V-brick), the topologies of which are controlled by the size of the pillar and nature of the included guest (size of the molecule and types of functional groups present in it). An interesting application of this work has consisted in the crystallization-based separation of isomeric mixtures of aromatic molecules,[34] and attempts have been made to use these systems for chiral discrimination.[37]

Yet, as described previously for guanidinium organomonosulfonates, the guanidinium sulfonate sheet structure of guanidinium organodisulfonates can be disrupted when solvent molecules capable of interacting with these sheets through hydrogen bonding are included in the structure. This turned out to be the case for guanidinium 1,5-naphthalenedisulfonate when it was crystallized in the presence of 2-methoxyethanol.[38] In another connection, the disulfonate anion can sometimes have other functions than just being a pillar between guanidinium sulfonate sheets; for instance, electrochemical studies have been carried out on guanidinium ferrocenedisulfonate that was adhered to a glassy carbon electrode.[39]

In recent years, our research efforts have focused on the preparation, characterization, and study of the polymerization behavior of symmetrical and unsymmetrical diacetylenes in which heteroelements are attached to the triple bonds.[40–44] In particular, it was found that 1,4-bis(triorganosilyl)buta-1,3-diynes and their tin-containing counterparts did not show any solid-state polymerization activity due to the bulkiness of the end-capping groups and the lack of strong interactions between molecules in the crystal lattice that could bring the C_4 rods near one another.[44] One way of improving this situation might consist of using guanidinium sulfonates containing a diacetylenic moiety, and this possibility is currently under investigation in our laboratory. In a parallel study, we decided to investigate guanidinium monoalkynesulfonates because these molecules are simpler models than the diacetylenic ones.[45] We report herein the synthesis and structural characterization of guanidinium sulfonates containing alkyne groups, that is, $[^{+}C(NH_2)_3][HC{\equiv}CSO_3^{-}]$ and $[^{+}C(NH_2)_3][CH_3C{\equiv}CSO_3^{-}]$. It was important to establish whether the 2D sheet structure found in guanidinium alkane- and arenesulfonates is maintained in these novel salts and determine what kind of arrangement is present in the third dimension. Our results show that a hydrogen-bonded sheet motif made of $R_2^2(8)$ and $R_6^3(12)$ rings is present in the solid-state structure of the ethyne derivative and that a sheet motif made of $R_2^1(6)$, $R_2^2(8)$ and $R_6^4(14)$ hydrogen-bonding interactions is present in the solid propyne derivative. The 3D structure of the propyne derivative is the same as that found in Ward's compounds, that is, it is a "typical" single-layer stacking motif. Interestingly, the 3D structure of the ethyne derivative is also a single-layer stacking motif, but it differs from that of the propyne derivative in that the alkynyl groups all point to the same side of the sheet. This unusual arrangement originates from interlayer hydrogen bonding between sulfonate anions.

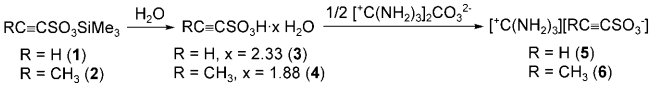
Results and Discussion

Syntheses: $HC{\equiv}CSO_3SiMe_3$ (**1**) is a known compound that was prepared in the past by sulfonation of $HC{\equiv}CSiMe_3$ with $ClSO_3SiMe_3$ or by sulfonation of $HC{\equiv}CSiMe_3$ with SO_3·dioxane;[46] we have synthesized **1** by using the former method (Scheme 2). $CH_3C{\equiv}CSO_3SiMe_3$ (**2**) was synthesized by sulfonation of $CH_3C{\equiv}CSiMe_3$ with SO_3·dioxane (Scheme 2). $ClSO_3SiMe_3$ and SO_3·dioxane were prepared as described in the literature.[46]



Scheme 2. Syntheses of compounds **1** and **2**.

Sulfonic acids $HC{\equiv}CSO_3H$ and $CH_3C{\equiv}CSO_3H$ were prepared by hydrolysis of **1** and **2**, respectively (Scheme 3). These acids were isolated as hydrates. ^1H NMR spectroscopy



Scheme 3. Syntheses of compounds **3**–**6**.

and elemental analysis showed the compositions of the two acids to be $HC{\equiv}CSO_3H{\cdot}2.33\,H_2O$ (**3**) and $CH_3C{\equiv}CSO_3H{\cdot}1.88\,H_2O$ (**4**). The composition of **3** is close to the $HC{\equiv}CSO_3H{\cdot}2.5\,H_2O$ stoichiometry found by Mérault.[46] The composition of **4** is similar to the $(CH_3)_3SiC{\equiv}CSO_3H{\cdot}2\,H_2O$ stoichiometry reported by Calas and Bourgeois.[47] The ethyne derivative $[^{+}C(NH_2)_3][HC{\equiv}CSO_3^{-}]$ (**5**) and propyne derivative $[^{+}C(NH_2)_3][CH_3C{\equiv}CSO_3^{-}]$ (**6**) were synthesized by allowing acids **3** and **4** to react with stoichiometric amounts of guanidinium carbonate (Scheme 3).

Molecular dimensions: X-ray quality crystals of **5** and **6** were obtained by dissolving these salts in water and allowing the solutions to evaporate slowly to dryness. It is worth noting that water molecules are not present in the structures

of **5** and **6**; this situation appears to be general and has been observed for most guanidinium monosulfonates described by Ward. This is presumably because the energy penalty for the disruption of the hydrogen-bond network of guanidinium sulfonates by water molecules is too high. However, one exception has been reported which is guanidinium 2,4-dinitrobenzenesulfonate monohydrate.[13,15]

Guanidinium 1-propynesulfonate (**6**) crystallizes in the centrosymmetric space group *Pnma* with $Z=12$ (see Table 1 in the Experimental Section). One molecule in the cell occupies a general position, and the other molecule lies on a mirror plane. The geometrical parameters of the crystallographically unique guanidinium cations and sulfonate groups are very much like those found in Ward's compounds: the C–N bond lengths are in the range 1.3195(12)–1.3269(10) Å and the N–C–N angles lie between 119.11(11) and 120.44(6)°. The S–O bond lengths span the range 1.4462(10)–1.4546(6) Å and the O–S–O angles the range 112.78(4)–113.31(4)°. The C≡C distances are those typically found in alkynes, that is, 1.1954(13) and 1.2062(18) Å. The S–C distances are 1.7086(9) and 1.7148(13) Å. The S–C≡C angles are close to 180° and so are the C≡C–CH_3 angles, that is, 177.22(9)° and 176.07(12)° for S–C≡C and 179.67(12)° and 178.90(15)° for C≡C-CH_3.

Guanidinium ethynesulfonate (**5**) crystallizes in the noncentrosymmetric space group $P6_3$ with $Z=6$ (see Table 1 in the Experimental Section). There is one crystallographically unique molecule in the cell. The geometrical parameters of the guanidinium cation are slightly different from those of **6**: there is one short C–N bond length (1.3232(12) Å) and two longer ones (1.3386(11) and 1.3460(12) Å), indicating a slight dissymmetry in the guanidinium cation. Although this situation is not common, it is not unusual and has been observed previously in the X-ray crystal structure of guanidinium methanesulfonate.[9] Slight differences are also observed in the N-C-N angles, one angle (117.95(6)°) being much smaller than the other two (119.20(4) and 119.63(3)°). The average N–C–N angle is 118.93°. The S–O bond lengths are slightly longer than those observed in **6** and span the range 1.4582(11)–1.4661(11) Å. The O–S–O angles are all smaller than those of **6**: 110.05(7), 111.19(7), and 111.55(6)°. The C≡C distance (1.194(2) Å) and S–C bond length (1.7169(19) Å) compare favourably with the values found in the 1-propynesulfonate salt. The S–C≡C angle (175.06(14)°) deviates slightly from the expected 180° value.

Two-dimensional structures: Unlike the situation commonly observed in guanidinium alkane- and arenesulfonates,[15] the guanidinium cations and sulfonate anions in solid **6** assemble into 1D ribbons through $R_2^2(8)$ and $R_2^1(6)$ dimer interactions (Figure 1). This is due to the fact that, in each ribbon, every third sulfonate anion has undergone a 60° rotation with respect to the two preceding ones. There are six unique N–H···O hydrogen bonds in each ribbon with geometries similar to those observed in Ward's compounds:[9–11] two of them are involved in a $R_2^1(6)$ dimer interaction and four of them in $R_2^2(8)$ interactions. The H···O distances in the $R_2^1(6)$ ring

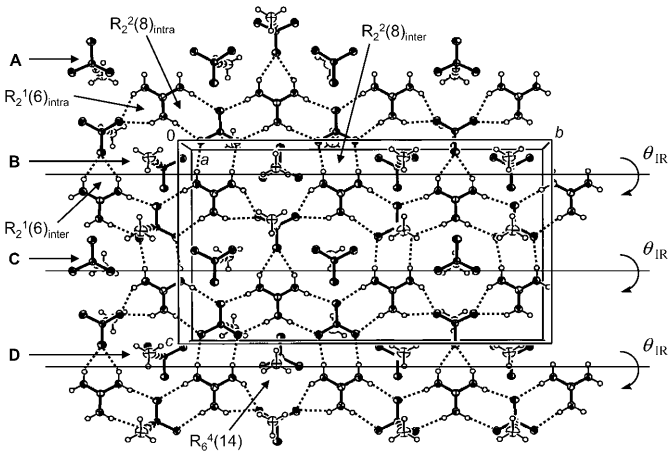


Figure 1. View along the *a* axis showing the hydrogen bond network in **6**. Ions connected through dotted lines belong to the main layer (*i* sheet). Rows of sulfonate anions labeled **A** and **C** belong to the $i+1$ sheet. Rows of sulfonate anions labeled **B** and **D** belong to the $i-1$ sheet.

are 2.16 (H(1A)···O(5)) and 2.14 Å (H(3A)···O(5)), and the corresponding N···O distances are 2.9437(11) (N(1)···O(5)) and 2.9315(11) Å (N(3)···O(5)). The N-H···O angles are alike but differ significantly from the optimum 180° value: ∢N(1)–H(1A)···O(5) = 148.1° and ∢N(3)–H(3A)···O(5) = 148.9°. The H···O distances in the $R_2^2(8)$ rings are 2.10 (H(1B)···O(1)), 2.15 (H(2B)···O(3)), 2.22 (H(4A)···O(3)), and 2.09 Å (H(5A)···O(2)). The corresponding N···O distances are 2.9727(19) (N(1)···O(1)), 3.0222(10) (N(2)···O(3)), 3.0685(10) (N(4)···O(3)), and 2.9645(8) Å (N(5)···O(2)). The N-H···O angles are 169.3° (N(1)–H(1B)···O(1)), 173.7° (N(2)–H(2B)···O(3)), 161.1° (N(4)–H(4A)···O(3)), and 173.2° (N(5)–H(5A)···O(2)). These angles are a lot closer to the optimum 180° angle, suggesting that hydrogen bonds involved in $R_2^2(8)$ dimer interactions are stronger than those involved in $R_2^1(6)$ interactions.

The guanidinium sulfonate ribbons assemble into 2D sheets through $R_2^1(6)$, $R_2^2(8)$ and $R_6^4(14)$ rings; typically observed $R_6^3(12)$ rings are not present. The hydrogen-bonded sheets lie in the *bc* plane. There are three unique interribbon hydrogen bonds: one of them is involved in a $R_2^1(6)$ dimer interaction and two of them in a $R_2^2(8)$ interaction. The hydrogen-bond length in the $R_2^1(6)$ ring is 2.17 Å (H(4B)···O(4)), and those in the $R_2^2(8)$ ring are 2.15 (H(2A)···O(1)) and 2.11 Å (H(3B)···O(2)). The corresponding N···O distances are 2.9467(12) (N(4)···O(4)), 3.0284(11) (N(2)···O(1)), and 2.9736(11) Å (N(3)···O(2)). The N–H···O angles are 146.3° (N(4)–H(4B)···O(4)), 172.8° (N(2)–H(2A)···O(1)), and 168.5° (N(3)–H(3B)···O(2)). Once again, hydrogen bonds involved in $R_2^2(8)$ dimer interactions appear to be stronger than those involved in $R_2^1(6)$ interactions, as indicated by the higher values of the N-H···O angles.

As seen in Figure 2, the alkynyl groups within a hydrogen-bonded sheet of **6** alternate orientation from one ribbon to the next; the stacking motif is thus single layer. This situation is unusual as it is generally observed for guanidinium organosulfonates with large R groups. The amount of puck-

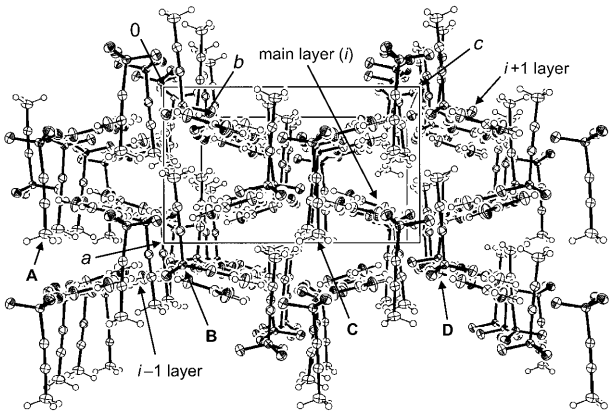


Figure 2. View along the *b* axis depicting the single-layer structure of **6**. Three layers are shown that are labeled *i*, *i*−1, and *i*+1. Rows of sulfonate anions marked **A**, **B**, **C**, and **D** are the same as in Figure 1.

ering of the sheets, as quantified by the dihedral angle θ_{IR} between the least-squares plane of one ribbon and the least-squares plane of an adjacent ribbon, is 151° ($\theta_{IR}=180°$ means no puckering). This low degree of puckering likely arises from the small steric demand of the alkynyl group. Guanidinium organosulfonates with similar θ_{IR} values and known to crystallize with a single-layer stacking motif include guanidinium 1-butanesulfonate (157°), guanidinium ferrocenesulfonate (153°), and guanidinium 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonate (165°).[9,11–13] Generally, guanidinium organosulfonates with a single-layer structure exhibit θ_{IR} angles that are much smaller (51–122°).[9,10,12,13]

The guanidinium cations and ethynesulfonate anions in solid **5** assemble into 1D ribbons through $R_2^2(8)$ dimer interactions, as is normally the case in guanidinium alkane- and arenesulfonates. The ribbons assemble into 2D sheets through $R_2^2(8)$ and $R_6^3(12)$ rings (Figure 3). There are six unique N–H···O hydrogen bonds in each sheet. The H···O distances are 2.10 (H(3B)···O(2)), 2.26 (H(2A)···O(3) and H(3A)···O(3)), 2.34 (H(2B)···O(1)), 2.36 (H(1B)···O(1)), and 2.50 Å (H(1A)···O(2)). The corresponding N···O distances are 2.9713(14) (N(3)···O(2)), 3.1348(15) (N(2)···O(3)), 3.1353(15) (N(3)···O(3)), 3.1464(19) (N(2)···O(1)), 3.2385(17) (N(1)···O(1)), and 3.3735(19) Å (N(1)···O(2)). The values of the N–H···O angles are all very similar except one: 170.4 (N(3)–H(3B)···O(2)), 171.5 (N(2)–H(2A)···O(3)), 172.2 (N(3)–H(3A)···O(3)), 152.5 (N(2)–H(2B)···O(1)), 174.9 (N(1)–H(1B)···O(1)), and 170.9° (N(1)–H(1A)···O(2)).

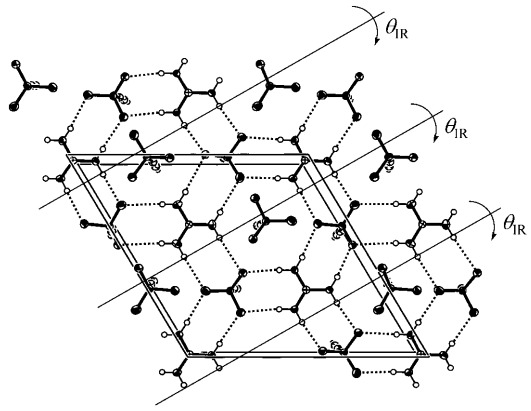


Figure 3. View along the *c* axis showing the hydrogen-bond network in **5**.

The alkynyl groups within a hydrogen-bonded sheet of **5** do not alternate sides from ribbon to ribbon. This stacking motif is reminiscent of a bilayer structure. However, the absence of polar regions between the sheets points to a single-layer structure. The hydrogen-bonded sheets of **5** lie in the *ab* plane (Figure 4). The amount of puckering is zero. A θ_{IR} angle of 180° has been observed in guanidinium methanesulfonate, guanidinium triflate, guanidinium ethanesulfonate, and guanidinium 2- and 3-nitrobenzenesulfonates; these salts all crystallize with a bilayer stacking motif.[9,12,13]

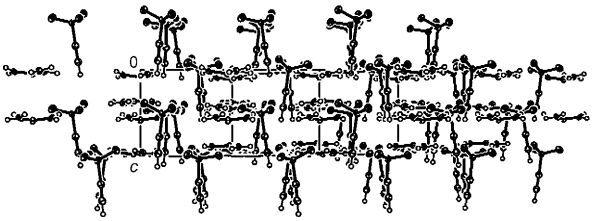


Figure 4. View perpendicular to the *c* axis showing the stacking of the layers in **5**.

Three-dimensional structures: The hydrogen-bonded sheets in **6** pile up along *a* with no polar region between the sheets, as is normally found in guanidinium organosulfonates with a single-layer structure (Figure 2). The sheets are highly interdigitated. The amount of interdigitation between the *i* and *i*−1 (or *i* and *i*+1) sheets, as estimated by adding the distance between the sulfur atom and the methyl carbon to the distance between the methyl carbon and the midpoint of the C≡C bond, amounts to 6.4 Å. The smallest separation between two successive (*i* and *i*+1, for instance) hydrogen-bonded sheets, roughly equivalent to the distance between the sulfur atom and the midpoint of the C≡C bond, is 2.3 Å. Consequently, no sizeable voids are present in the solid and a compact structure is obtained ($\rho_{calcd}=1.474\ g\,cm^{-3}$). This arrangement is also an ideal one to maximize N–H···π interactions between guanidinium cations and acetylenic moieties. Indeed, close examination of the X-ray crystal structure indicates that there are numerous N–H···π contacts (Figure 5). There are eighteen $H_{guanidinium}\cdots C_{sp}$ distances ranging from 2.6766 to 3.1540 Å, and twelve of them are below 3 Å. The N–H···C_{sp} angles span the range 92.10–116.54°. Clearly, these interactions are weak. However, their large number suggests that their contribution to stabilization of the structure is not negligible. Literature concerning N–H···C≡C interactions in small molecules is scarce. Yet, such an interaction has been observed in 1-(2′-aminophenyl)-2-(2″-nitrophenyl)ethyne.[4,48] In this compound, one amino hydrogen interacts with the nearby triple bond. It is an in-

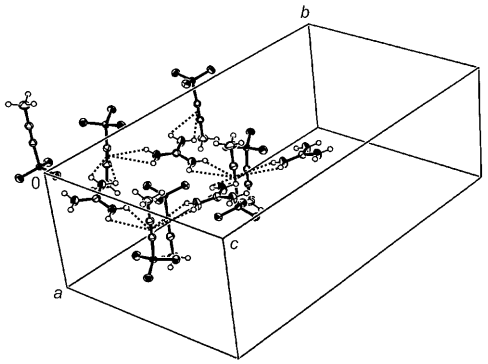


Figure 5. View showing N–H···π interactions (dashed lines) in crystalline **6**.

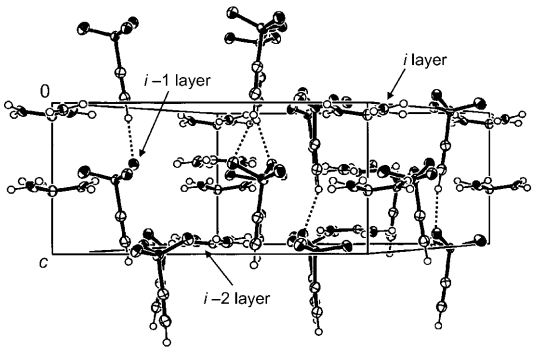


Figure 6. View perpendicular to the *c* axis showing C_{sp}–H···O contacts (dashed lines) between sulfonate anions from the *i* and *i*–2 layers in crystalline **5**.

tramolecular N–H···C≡C hydrogen bond bifurcated by an intramolecular N–H···O_2N interaction. The N–H···C_{sp} distances are 2.38 and 2.72 Å and the distance between the hydrogen and the midpoint of the C≡C bond is 2.49 Å; the angle between the N–H direction and an axis passing through the N–H hydrogen and the center of the C≡C bond is 117°.[4] Thus, the N–H···C_{sp} distances in **6** are longer than those observed in 1-(2′-aminophenyl)-2-(2″-nitrophenyl)-ethyne and the N–H···C_{sp} angles are smaller, suggestive of weaker N–H···C≡C interactions in the former compound.

Other interdigitation schemes are possible that were not observed in the solid-state structure of **6** for the following reasons: the first possibility is that the sheets are not interdigitated at all. This situation would be unfavourable because large voids would be created in the structure and steric repulsion between methyl groups in the nonpolar region between the sheets would be substantial. The second conceivable situation is that the amount of interdigitation is half the length of the 1-propynesulfonate anion, that is, 2.2 Å. In this case, voids in the structure would be reduced and steric repulsion between methyl groups would be nil. However, this situation would not take advantage of the stabilizing N–H···C≡C interactions mentioned earlier. A third possible scenario is that the amount of interdigitation is equal to the full length of the 1-propynesulfonate anion, that is, 4.4 Å. In this case, the sheet structure would be disrupted because the methyl groups would be interfering with the guanidinium sulfonate hydrogen-bond network.

The 3D structure of **5** is also single layer, because there is no polar region between the sheets (Figure 4). The hydrogen-bonded sheets all have ethynyl moieties pointing in the same direction; there is no up-down-up-down alternation. The structure may be regarded as a bilayer structure in which every other layer has been turned around. The hydrogen-bonded sheets pile up along *c*. The amount of interdigitation between the *i* and *i*–1 sheets is quite small and is estimated to be about 1 Å, that is, the length of the C_{sp}–H bond. The cause of this unusual situation is evident from Figure 6: every sulfonate anion from an *i* layer interacts through a C_{sp}–H···O hydrogen bond with another sulfonate anion located in the *i*–2 sheet. The C_{sp}–H···O(sulfonate) hydrogen-bond length is 2.35 Å and the C_{sp}···O distance 3.241(2) Å. The C_{sp}–H···O angle is 156.3°. These geometrical parameters compare well with the values found in the literature: a CSD analysis indicates that the mean C_{sp}–H···O distance is 2.40(2) Å and the mean C_{sp}···O distance 3.35(1) Å.[49] The C_{sp}–H···O angles cluster in the range 150–160°.[50,51] It is worth noting that C≡C–H···C≡C interactions as those observed in simple alkynes are not present.[52] Evidently, the structure of **5** is governed by the guanidinium sulfonate sheet motif.

Conclusions

In summary, it has been shown that [$^+$C(NH$_2$)$_3$][HC≡CSO$_3^-$] (**5**) and [$^+$C(NH$_2$)$_3$][CH$_3$C≡CSO$_3^-$] (**6**) both crystallize with a single-layer structure. Hence, the hydrogen-bonded sheet motif observed previously in guanidinium alkane- and arenesulfonates is maintained when the organosulfonate R group is changed for an alkyne group. As found in other guanidinium sulfonate salts, the robust N–H···O(sulfonate) hydrogen-bond network controls the packing of the molecules. Interactions such as N–H···C≡C and C_{sp}–H···O are too weak to disrupt this network, unlike the situation observed in systems possessing substituents with strong hydrogen-bonding capabilities.[10,13] Yet, it was found that these weak interactions were capable of bringing subtle changes to the basic arrangement: in the case of **6**, a compact structure is obtained in which the sheets are highly interdigitated due to the presence of numerous N–H···C≡C contacts. In the case of **5**, the hydrogen-bonded sheets all have ethynyl moieties pointing in the same direction, because of interlayer C_{sp}–H···O interactions between organosulfonate anions. On the basis of Desiraju's classification, the latter hydrogen bond may be regarded as intrusive.[5] In effect, the structure of **5** is reminiscent of some work published by Janiak in which an "inverse bilayer" structure was observed for a series of 1,1′-binaphthalene-2,2′-diyl phosphate salts.[53] This unusual situation was ascribed to hydrogen bonding from the cations and solvent molecules to the hydrophilic (RO)$_2$PO$_2^-$ phosphate heads that creates an interior hydrophilic region and

exposes the binaphthyl groups on both exterior sides. The present study is currently being extended to guanidinium disulfonates bearing alkyne and diacetylenic groups to see how these salts compare with guanidinium α,ω-alkane- and arenedisulfonates. Also, work is underway to see if other weak interactions such as arene···perfluoroarene have structure-modifying abilities similar to those of the N−H···C≡C and C_{sp}−H···O(sulfonate) interactions reported here.

Experimental Section

General considerations: Solution-phase ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker Avance DPX 200 spectrometer. ^{13}C NMR spectra were obtained on either one of the following Bruker instruments: Avance DPX 200, AC 250, Avance DRX 400. ^{1}H chemical shifts were referenced to the protio impurity of the NMR solvent, ^{13}C chemical shifts were referenced to the NMR solvent, and ^{29}Si NMR chemical shifts were referenced to tetramethylsilane. Infrared spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer with a 4 cm^{-1} resolution. Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. FAB mass spectra were obtained on JEOL JMS-SX102 A and JEOL JMS-DX300 instruments. HRMS measurements were performed on a Varian MAT 311 double-focusing mass spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes I, Rennes (France), by using electron impact (70 eV) as the ionization mode. Elemental analyses were carried out at the Service Central de Microanalyse of the Centre National de la Recherche Scientifique (CNRS), Vernaison (France).

Materials: (Trimethylsilyl)acetylene (98%) was purchased from Lancaster (Eastgate, England) and 1-trimethylsilyl-1-propyne (97%) from Alfa Aesar (Karlsruhe, Germany). Guanidinium carbonate (99%) was obtained from Aldrich (Steinheim, Germany) and used as supplied. 1,4-Dioxane (extra dry, with molecular sieves, H_2O <50 ppm, stabilized) and H_2O (HPLC gradient grade) were purchased from Acrõs Organics (Geel, Belgium). CH_2Cl_2 was distilled over CaH_2 prior to use. $ClSO_3SiMe_3$ and SO_3·dioxane were prepared as described in the literature.[46]

Synthesis of HC≡CSO$_3$SiMe$_3$ (1): Alkyne **1** was synthesized by sulfonation of HC≡CSiMe$_3$ with $ClSO_3SiMe_3$ as described by Mérault.[46]

Synthesis of CH$_3$C≡CSO$_3$SiMe$_3$ (2): Alkyne **2** was synthesized by sulfonation of CH$_3$C≡CSiMe$_3$ with SO_3·dioxane by following a procedure adapted from Mérault.[46] After completion of the reaction, the volatiles were removed, and the crude product was purified by vacuum distillation (50°C, 0.05 mbar). A colorless viscous liquid was obtained. Yield: 80%; ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.49 (s, 9H; Si(CH$_3$)$_3$), 2.10 ppm (s, 3H; CH$_3$C≡); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = −0.2 (Si(CH$_3$)$_3$), 3.3 (CH$_3$), 74.5 (≡CSO$_3$), 88.3 ppm (CH$_3$C≡); ^{29}Si NMR (39.8 MHz, $CDCl_3$): δ = 35.8 ppm (Si(CH$_3$)$_3$); IR (CCl_4): $\tilde{\nu}$ = 2960 (w; C(sp^3)−H), 2917 (w; C-(sp^3)−H), 2852 (w; C(sp^3)−H), 2225 (s; C≡C), 1373 (s; SO_2), 1259 (vs; Si-CH$_3$), 1187 cm^{-1} (vs; SO_2); HRMS (EI): *m*/*z* calcd for $C_5H_9O_3SSi^+$: 177.00417 [*M*−CH$_3$]$^+$; found: 177.0045; elemental analysis calcd (%) for $C_6H_{12}O_3SSi$ (192.3045): C 37.47, H 6.29, S 16.67; found: C 35.30, H 5.74, S 17.6.

Synthesis of HC≡CSO$_3$H·2.33 H$_2$O (3): A portion of deionized H_2O (7 mL) was added to a solution of **1** (12.5 g, 70 mmol) in Et_2O (10 mL). The two-phase mixture was stirred overnight. The two layers were separated, and the aqueous layer was washed with Et_2O (3×20 mL) to remove completely the hexamethyldisiloxane that was formed in the reaction. The aqueous layer was concentrated on a rotary evaporator, then heated to 79°C on a vacuum line. The residual liquid was left to stand at RT, during which time a solid formed. ^{1}H NMR spectroscopy and elemental analysis showed the amount of H_2O per mole of sulfonic acid to be 2.33, which is close to the HC≡CSO$_3$H·2.5 H$_2$O composition reported by Mérault.[46] The solid is hygroscopic and turns into a liquid upon exposure to air over a period of several days. Yield: 74%; ^{1}H NMR (200.1 MHz, [D$_6$]DMSO): δ = 3.60 (s, 1H; HC≡), 7.64 ppm (s, 5.66H; SO_3H+H_2O); ^{13}C NMR (62.9 MHz, [D$_6$]DMSO): δ = 69.8 (HC≡), 85.6 ppm (≡CSO$_3$); IR (nujol): $\tilde{\nu}$ = 3272 (s; ≡C−H), 2085 (s; C≡C), 1213 (vs; SO_3), 1055 cm^{-1} (s; SO_3); HRMS (EI): *m*/*z* calcd for $C_2H_2O_3S^+$: 105.97247 [*M*]$^+$; found: 105.9722; elemental analysis calcd (%) for $C_2H_2O_3S$·2.33 H_2O (148.0714): C 16.22, H 4.53, O 57.59, S 21.65; found: C 16.70, H 4.25, O 57.29, S 21.98.

Synthesis of CH$_3$C≡CSO$_3$H·1.88 H$_2$O (4): An Erlenmeyer flask containing **2** (2.91 g, 15.1 mmol) was left open in a freezer at −10°C over a period of 3 d. The hydrolyzed material was allowed to come to RT, then a portion of deionized H_2O (20 mL) was added. The aqueous layer was washed with Et_2O (3×20 mL) to remove completely the hexamethyldisiloxane that was formed in the reaction. The aqueous layer was concentrated on a rotary evaporator. A brown viscous liquid was obtained for which ^{1}H NMR spectroscopy and elemental analysis established that the composition was CH$_3$C≡CSO$_3$H·1.88 H$_2$O. Yield: 96%; ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.12 (s, 3H; CH$_3$), 9.91 ppm (s, 4.76H; SO_3H+H_2O); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 3.3 (CH$_3$), 79.8 (CH$_3$*C*≡), 81.2 ppm (≡CSO$_3$); IR (neat): $\tilde{\nu}$ = 2926 (w; C(sp^3)−H), 2222 (vs; C≡C), 1132 (vs; SO_3), 1057 cm^{-1} (vs; SO_3); FAB-MS negative ion mode (GT): *m*/*z* (%): 119 (39) [CH$_3$C≡CSO$_3^-$]; elemental analysis calcd (%) for $C_3H_4O_3S$·1.88 H_2O (153.991): C 23.40, H 5.08, S 20.82; found: C 23.22, H 5.39, S 20.97.

Synthesis of [$^+$C(NH$_2$)$_3$][HC≡CSO$_3^-$] (5): Compound **5** was synthesized by dissolving and stirring stoichiometric amounts of sulfonic acid **3** (5.92 g, 40 mmol) and guanidinium carbonate (3.6 g, 20 mmol) in H_2O (60 mL). A dark powder was obtained upon removal of the solvent. The crude product was decolorized with activated charcoal and recrystallized from an EtOH/Et_2O mixture to give a pale yellow powder. Yield = 79%; m.p. 113.6–129.7°C; ^{1}H NMR (200.1 MHz, [D$_6$]DMSO): δ = 3.66 (s, 1H; HC≡), 6.88 ppm (s, 6H; $^+$C(NH$_2$)$_3$); ^{13}C NMR (62.9 MHz, [D$_6$]DMSO): δ = 69.6 (HC≡), 85.9 (≡CSO$_3$), 157.7 ppm ($^+$C(NH$_2$)$_3$); IR (KBr): $\tilde{\nu}$ = 3404 (br; NH), 3237 (s; NH), 3154 (s; NH), 2073 (s; C≡C), 1662 (vs; CN$_3$ + NH$_2$), 1231 (vs; SO_3), 1064 cm^{-1} (s; SO_3); FAB-MS positive ion mode (GT): *m*/*z* (%): 225 (47) [($^+$C(NH$_2$)$_3$)$_2$(HC≡CSO$_3^-$)]$^+$, 60 (100) [$^+$C-(NH$_2$)$_3$]; FAB-MS negative ion mode (GT): *m*/*z* (%): 270 (17) [($^+$C-(NH$_2$)$_3$)(HC≡CSO$_3^-$)$_2$]$^-$, 105 (100) [HC≡CSO$_3^-$]; elemental analysis calcd (%) for $C_3H_7N_3O_3S$ (165.1666): C 21.82, H 4.27, N 25.44, O 29.06, S 19.41; found: C 21.23, H 4.08, N 22.06, O 30.47, S 19.13.

Synthesis of [$^+$C(NH$_2$)$_3$][CH$_3$C≡CSO$_3^-$] (6): Sulfonic acid **4** (0.55 g, 3.6 mmol) was reacted with guanidinium carbonate (0.32 g, 1.8 mmol) in H_2O (5 mL) by following the same procedure as that used to prepare **5** (see above). Recrystallisation of the crude product from an EtOH/Et_2O mixture gave a white powder. Yield = 85%; m.p. 138–182°C; ^{1}H NMR (200.1 MHz, [D$_6$]DMSO): δ = 1.84 (s, 3H; CH$_3$), 6.98 ppm (s, 6H; $^+$C-(NH$_2$)$_3$); ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 3.5 (CH$_3$), 78.4 (CH$_3$*C*≡), 82.6 (≡CSO$_3$), 158.7 ppm ($^+$C(NH$_2$)$_3$); IR (KBr): $\tilde{\nu}$ = 3419 (br; NH), 3271 (s; NH), 3201 (s; NH), 2223 (s; C≡C), 1659 (vs; CN$_3$+NH$_2$), 1229 (vs; SO_3), 1065 cm^{-1} (s; SO_3); FAB-MS positive ion mode (GT): *m*/*z* (%): 239 (34) [($^+$C(NH$_2$)$_3$)$_2$(CH$_3$C≡CSO$_3^-$)]$^+$, 60 (100) [$^+$C(NH$_2$)$_3$]; FAB-MS negative ion mode (GT): *m*/*z* (%): 298 (46) [($^+$C(NH$_2$)$_3$)(CH$_3$C≡CSO$_3^-$)$_2$]$^-$, 119 (100) [CH$_3$C≡CSO$_3^-$]; elemental analysis calcd (%) for $C_4H_9N_3O_3S$ (179.1934): C 26.81, H 5.06, N 23.45, O 26.79, S 17.89; found: C 26.14, H 5.37, N 22.93, O 26.75, S 18.20.

X-ray diffraction: Single-crystals of **5** and **6** were grown from H_2O. X-ray diffraction experiments were carried out on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cryostream Cooler Device. Intensity data were collected at 180 K in both cases. The crystal-to-detector distance was 70 mm for both measurements. For **5**, a total of 179 exposures (4 min per exposure) were taken with 0 < ϕ < 250.6° and crystal oscillations of 1.4° in ϕ.[54] For **6**, 139 exposures (5 min per exposure) were taken with 0 < ϕ < 250.2° and crystal oscillations of 1.8° in ϕ. No decay corrections were made to the data based on intensity checks of two hundred control reflections. The cell parameters were refined from 8000 reflections. Owing to the low values of μ, no absorption corrections were made.

Both structures were solved by direct methods (SHELXS-97).[55] The SHELXL-97 program was used for full-matrix least-squares refinement against F_o^2 by using all reflections.[56] Atomic scattering factors were

taken from a standard source.[57] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in the calculations with the riding model, with isotropic thermal parameters equal to 1.1-times that of the atom of attachment. Final R values and relevant crystallographic data are given in Table 1.

Table 1. Crystal data and experimental details of data collection and refinement for **5** and **6**.

	5	**6**
formula	$C_3H_7N_3O_3S$	$C_4H_9N_3O_3S$
M_r	165.18	179.20
crystal color	colorless	colorless
crystal size [mm]	$0.45\times0.30\times0.25$	$0.50\times0.45\times0.20$
crystal system	hexagonal	orthorhombic
space group	$P6_3$ (No. 173)	$Pnma$ (No. 62)
a [Å]	13.4466(11)	7.9199(8)
b [Å]	13.4466(11)	23.304(2)
c [Å]	6.6927(5)	13.1285(14)
α [°]	90	90
β [°]	90	90
γ [°]	120	90
V [Å^3]	1047.99(14)	2423.0(4)
Z	6	12
ρ_{calcd} [g cm^{-3}]	1.570	1.474
$F(000)$	516	1128
μ [mm^{-1}]	0.416	0.366
T [K]	180	180
λ [Å]	0.71073	0.71073
2θ range [°]	3.3–52.1	3.3–52.1
index ranges	$-16\le h\le16$ $-16\le k\le16$ $-7\le l\le7$	$-9\le h\le9$ $-28\le k\le28$ $-16\le l\le16$
reflections collected	10375	21777
independent reflections	1309	2435
R_{int} (on I)	0.0258	0.0252
obsd reflections $[F_o>4\sigma(F_o)]$	1226	2240
parameters	91	160
goodness-of-fit on F_o^2 (all reflns)	1.064	1.198
w[a]	$[\sigma^2(F_o^2)+(0.0283P)^2]^{-1}$	$[\sigma^2(F_o^2)+0.2076P]^{-1}$
max/mean shift/esd	0.000/0.000	0.001/0.000
R[b]/R_w[c] (obsd reflns)	0.0200/0.0425	0.0180/0.0358
R[b]/R_w[c] (all reflns)	0.0205/0.0425	0.0190/0.0360
largest diff. peak/hole [e Å^{-3}]	0.127/−0.123	0.159/−0.160

[a] $P=(F_o^2+2F_c^2)/3$. [b] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c] $R_w=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

CCDC-735562 (**5**) and 735561 (**6**) 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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