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The solid-state structures of guanidinium sulfonates, $[C(NH_2)_3]^+ RSO_3^-$, are being studied and the role of hydrogen bonding in controlling molecular packing assessed. We have found that guanidinium sulfonates frequently self-assemble into two-dimensional sheets formed by hydrogen bonds between the six guanidinium protons and the six sulfonate oxygen lone electron pairs. X-ray structures of guanidinium methanesulfonate, guanidinium ethanesulfonate, and guanidinium triflate are reported here. Each of these salts crystallizes in a bilayer structure of hydrogen-bonded sheets.

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Technical Report #20

**"Solid-State Structures of Guanidinium Methane-, Ethane-, and
Trifluoromethanesulfonate"**

by

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Control of packing in the solid-state is instrumental in the design of molecular materials. Hydrogen bonds, one of strongest intermolecular interactions, can be used to direct crystal packing. We have discovered that guanidinium sulfonates, $[\text{C}(\text{NH}_2)_3]^+ \text{RSO}_3^-$, frequently pack by forming two-dimensional sheets of hydrogen bonds between the six guanidinium protons and the six sulfonate oxygen lone electron pairs (Figure 1). This is important for materials design because crystal packing is strongly and reproducibly controlled in two dimensions. Guanidinium methanesulfonate and guanidinium ethanesulfonate are isostructural and crystallize in monoclinic space group $C2/m$. Guanidinium trifluoromethanesulfonate (triflate) has a similar structure, but crystallizes in monoclinic space group $C2/c$. Crystallographic data for the three salts is given in Table I.

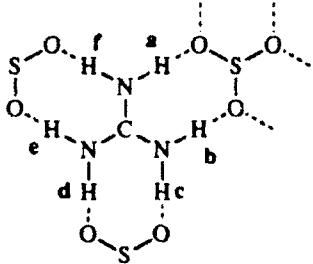
Table I. Crystallographic Data for Guanidinium Salts of Methanesulfonate, Ethanesulfonate, and Triflate.

compound	guanidinium methanesulfonate	guanidinium ethanesulfonate	guanidinium triflate
formula	$\text{C}_2\text{H}_9\text{N}_3\text{O}_3\text{S}$	$\text{C}_3\text{H}_{11}\text{N}_3\text{O}_3\text{S}$	$\text{C}_2\text{H}_6\text{F}_3\text{N}_3\text{O}_3\text{S}$
FW	155.17	169.20	209.14
crystal color, habit	col, plate	col, plate	col, plate
crystal size (mm)	0.700 x 0.500 x 0.100	0.550 x 0.450 x 0.170	0.550 x 0.450 x 0.150
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/m$	$C2/m$	$C2/c$
a (Å)	12.778 (5)	12.793 (4)	12.988 (7)
b (Å)	7.342 (2)	7.398 (5)	7.512 (2)
c (Å)	9.998 (2)	11.172 (3)	18.45 (1)
β (°)	126.96 (2)	128.060 (2)	111.69 (4)
V (Å ³)	749.6 (8)	833 (1)	1672 (3)
Z	4	4	8
D_x (g/cm ³)	1.375	1.350	1.661
F (000)	328	360	848
μ (MoK α) (cm ⁻¹)	3.66	3.35	3.99
T (°C)	24	24	24
no. data ($F_0 > 2\sigma(F_0)$)	743	749	1284
R	0.051	0.058	0.038
R_w	0.079	0.072	0.053
$2\theta_{\text{max}}$ (°)	51.9	56.0	51.9
range of hkl	$\pm 15, +9, \pm 12$	$\pm 16, +9, \pm 14$	$\pm 12, +7, \pm 17$
(shift/error) _{max}	0.02	0.02	0.04
largest peak (e ⁻ /Å ³)	0.48	0.33	0.28
GOF	2.33	1.50	1.36

Each structure is composed of two-dimensional guanidinium-sulfonate hydrogen-bonded sheets in approximately the ab plane. The N...O distances of the hydrogen bonds are given in Table II. Figure 2 shows a view normal to the guanidinium ions of one hydrogen-bonded layer in guanidinium methanesulfonate; analogous packing occurs in the guanidinium salts of ethanesulfonate and triflate. The hydrogen-bond sheets pack in bilayer structures (Figure 3) in which the sulfonate R groups (methyl, ethyl, or trifluoromethyl) are all oriented to one side of each sheet, resulting in partitioning into hydrophobic and hydrophilic regions. Guanidinium ethanesulfonate is isostructural to guanidinium methanesulfonate; the cell parameters a , b , and β are equivalent to those in guanidinium methanesulfonate, with the c constant (direction approximately normal to the hydrogen-bond sheet) lengthening (11.172 versus 9.998 Å) to accommodate packing of

the slightly larger ethyl group. Guanidinium triflate packs slightly differently; the mirror symmetry element is replaced by a glide in this structure. We believe that the difference in packing arises from an electronic effect due to the fluorine atoms of the triflate. The controlled crystal packing in two dimensions in these salts suggests that further engineering in the third dimension will lead to new materials with desirable properties such as second-order nonlinear optical activity.

Table II. N...O Distances (Å) in guanidinium methanesulfonate, ethanesulfonate, and triflate.



hydrogen bond	guanidinium methanesulfonate	guanidinium ethanesulfonate	guanidinium triflate
a	2.893 (2)	2.927 (3)	2.985 (4)
b	2.917 (3)	2.957 (4)	2.990 (4)
c	2.935 (3)	2.957 (3)	2.986 (3)
d	= c	= c	2.992 (3)
e	= b	= b	2.998 (3)
f	= a	= a	3.001 (3)

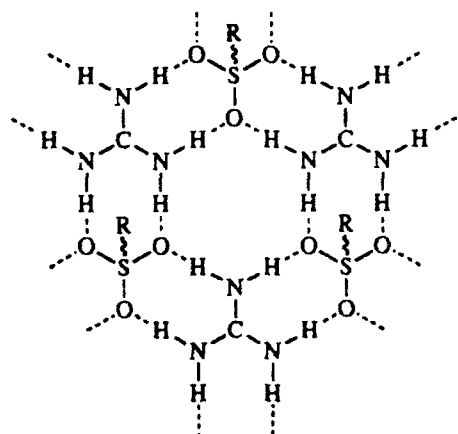


Figure 1. Common hydrogen-bond pattern in guanidinium sulfonates.

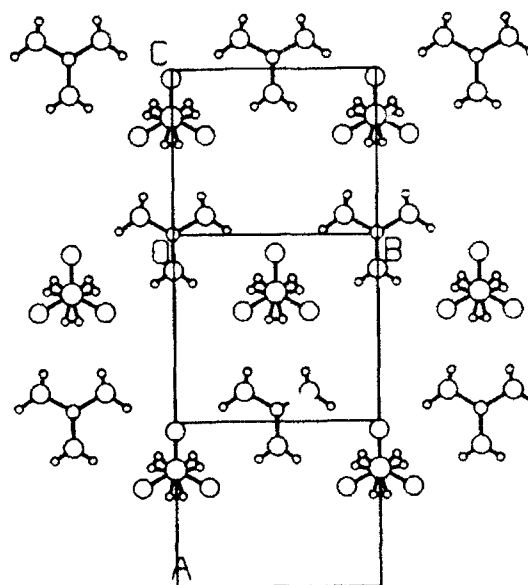
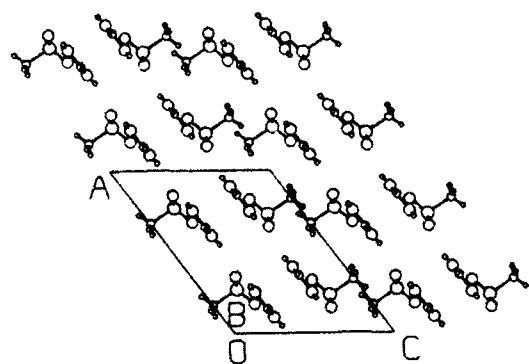
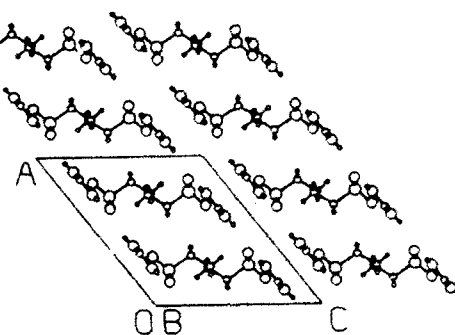


Figure 2. View normal to guanidinium ions of one hydrogen-bond layer in guanidinium methanesulfonate.

a



b



c

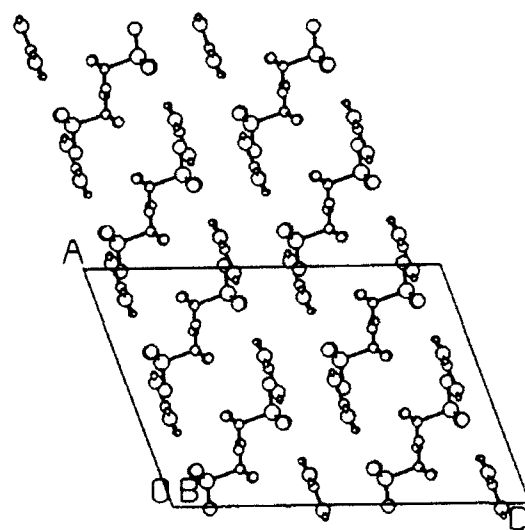


Figure 3. Bilayer structures in (a) guanidinium methanesulfonate, (b) guanidinium ethanesulfonate, and (c) guanidinium triflate.

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