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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Guanidinium p-nitro- and p-hydroxybenzenesulfonate crystallize in noncentrosymmetric (acentric) space groups and exhibit second-harmonic generation. The engineering of these structures was accomplished using hydrogen bonding and the tendency to pack in centrosymmetric structures overcome by screening of the dipolar forces between arylsulfonates by charged layers of guanidinium ions.				
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Technical Report #24

**"Design of Acentric Materials: X-ray Structures of Guanidinium
p-Nitro- and *p*-Hydroxybenzenesulfonate"**

by

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The X-ray crystal data for guanidinium *p*-nitrobenzenesulfonate follows: $C_7H_{10}N_4O_5S$, $M_r = 262.24$, orthorhombic, *Ama*2, $a = 7.471$ (8), $b = 20.690$ (7), $c = 7.340$ (2) Å, $V = 1135$ (2) Å³, $Z = 4$, $D_{calc} = 1.535$ g/cm³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 2.89$ cm⁻¹, $F(000) = 544$, $T = 297$ K, $R = 0.048$, $R_w = 0.047$ for 1165 observed reflections. The structure is composed of sheets of *p*-nitrobenzenesulfonate anions in the *bc* plane linked by guanidinium sulfonate hydrogen-bonding interactions. The nitro group and one sulfonate oxygen atom are coplanar with the aromatic ring. The anion layers are related by two-fold axes and A-centering; each anion layer is offset from neighboring layers by about 90°. The X-ray structure of guanidinium *p*-hydroxybenzenesulfonate is similar, but is body-centered rather than A-centered. X-ray data follows: $C_7H_{11}N_3O_4S$, $M_r = 233.24$, orthorhombic, *Ima*2, $a = 7.191$ (4), $b = 17.345$ (5), $c = 7.899$ (3) Å, $V = 985$ (1) Å³, $Z = 4$, $D_x = 1.572$ g/cm³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 3.13$ cm⁻¹, $F(000) = 488$, $T = 297$ K, $R = 0.035$, $R_w = 0.047$ for 635 unique observed reflections. As in guanidinium *p*-nitrobenzenesulfonate the structure is composed of sheets of anions linked by hydrogen bonding. Stereoviews of the crystal packing each salt are given in Figures 2 and 3.

Hydrogen-bond geometries of both salts are given in Table I. The hydrogen bonding in guanidinium *p*-nitrobenzenesulfonate is slightly different than predicted. We expected this salt to crystallize with hydrogen-bond sheets (Figure 1) arranged in bilayers, as found in guanidinium *p*-toluenesulfonate, due to the relatively poor accepting ability of the nitro oxygens compared to the sulfonate oxygens. We found, however, that a different hydrogen bond pattern occurs in this structure. Hydrogen-bonded ribbons of four guanidinium-sulfonate hydrogen-bond interactions identical to those found in previous structures occur in guanidinium *p*-nitrobenzenesulfonate. Each ribbon is linked to a neighboring ribbon through two similar guanidinium sulfonate hydrogen bonds; i.e. the two remaining guanidinium protons interact with the two remaining oxygen lone pairs with the guanidinium ion approximately perpendicular to the plane of the three sulfonate oxygens on a neighboring ribbon, rather than in approximately the same plane as in guanidinium *p*-toluenesulfonate. These six interactions make up a distorted hydrogen-bonded single layer structure in the *z*-direction (see Figure 2). Hydrogen bonding to nitro groups does not occur although there may be a weak bifurcated interaction between one nitro oxygen atom and two mirror-related guanidinium protons attached to the same nitrogen atom, with N...O 3.192 (6) and H...O 2.90 (3) Å.

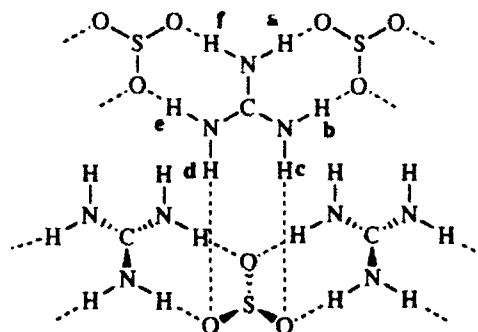
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In guanidinium *p*-hydroxybenzenesulfonate hydrogen-bonded ribbons of four guanidinium-sulfonate hydrogen bonds occur as in guanidinium *p*-nitrobenzenesulfonate. The ribbons are not linked to one another through hydrogen bonding, however. Although the hydroxyl proton was not found in the X-ray analysis, it seems to be located in a position to maximize a number of weak interactions. A bifurcated weak interaction takes place between the phenolic oxygen atom and the remaining two guanidinium protons of length $N\cdots O_{\text{hydroxy}} = 3.188(4) \text{ \AA}$ and angle 139.71° . No hydrogen bonding occurs between the remaining sulfonate oxygens and the hydroxy proton as evidenced by no $O\cdots O$ distances less than $3.6 \text{ \AA}$. An arrangement similar to the single layer structure found in the *p*-nitrobenzenesulfonate salt can be seen in the *c*-direction. The difference in guanidinium-sulfonate hydrogen bonding in this structure compared to the fully hydrogen-bonded pattern found in previous structures results from competitive hydrogen bonding with the hydroxyl group. The hydroxyl proton is a better hydrogen bond donor than guanidinium proton and so would be expected to hydrogen bond to the best acceptor (sulfonate oxygen) as per our general hydrogen bond rule of best donor hydrogen bonding to best acceptor.

Both structures are noncentrosymmetric with all nitro or hydroxyl groups oriented in one direction. Both exhibit second harmonic generation, guanidinium *p*-nitrobenzenesulfonate about $0.75 \times$ urea and guanidinium *p*-hydroxybenzenesulfonate about $0.5 \times$ urea. We have successfully engineered the structures of these two salts into noncentrosymmetric arrangements using hydrogen bonding interactions. Our findings will be applied to the design of other novel noncentrosymmetric molecular materials.

Table I. Hydrogen Bond Geometries in Guanidinium *p*-Nitro- and *p*-Hydroxybenzenesulfonate.



hydrogen bond	guanidinium <i>p</i> -nitrobenzenesulfonate		guanidinium <i>p</i> -hydroxybenzenesulfonate	
	N...O distance (Å)	N-H...O angle (°)	N...O distance (Å)	N-H...O angle (°)
a	2.900 (4)	177.48	2.938 (4)	174.49
b	3.005 (5)	174.26	2.955 (3)	168.81
c	3.018 (4)	169.21	> 3.6	
d	= c	= c	= c	= c
e	= b	= b	= b	= b
f	= a	= a		

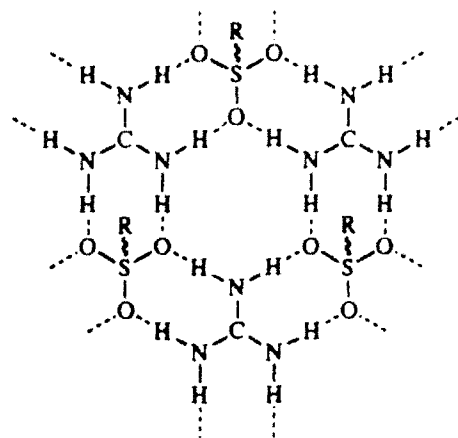


Figure 1. Common hydrogen-bond pattern in guanidinium sulfonates.

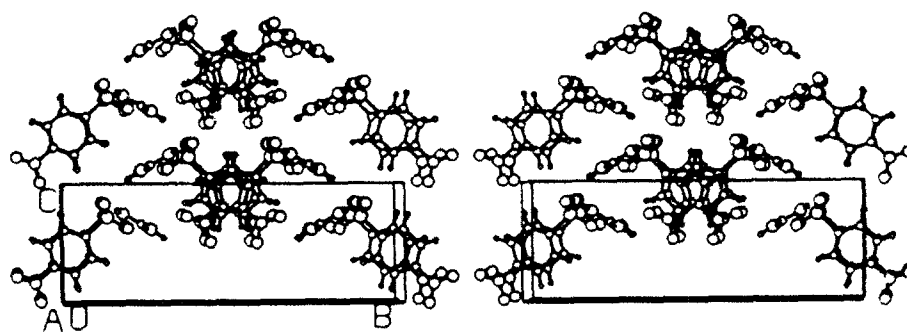


Figure 2. Stereoview along the *x*-axis in guanidinium *p*-nitrobenzenesulfonate.

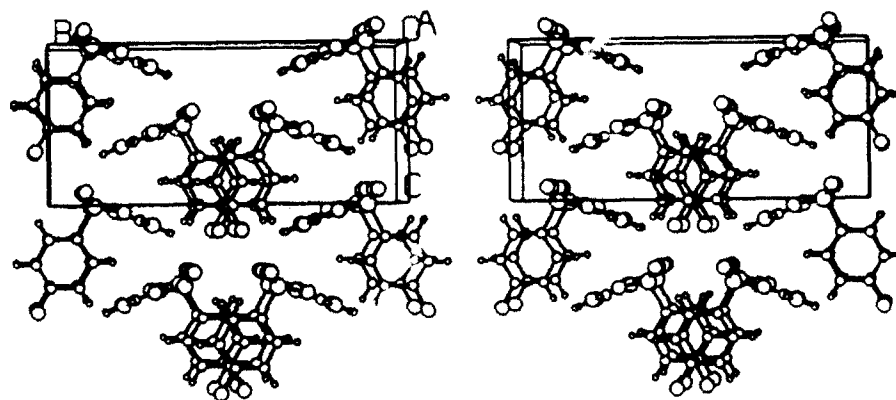


Figure 3. Stereoview along the *x*-axis in guanidinium *p*-hydroxybenzenesulfonate.

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