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Hydrogen bonding is used to direct guanidinium sulfonates, $[C(NH_2)_3]^+RSO_3^-$, into specific molecular packing arrangements in the solid state. 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. Guanidinium 4-biphenylsulfonate crystallizes in two polymorphic forms, differing only slightly in their hydrogen bonding patterns. We report on the synthesis of these polymorphs and their characterization by FTIR spectroscopy and single crystal X-ray diffraction.

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"Hydrogen-Bond Polymorphs of Guanidinium 4-Biphenylsulfonate"

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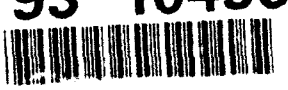
April 22, 1993



Guanidinium 4-biphenylsulfonate was prepared as part of an investigation of the molecular packing modes of guanidinium with aryl sulfonates, C_6H_5-$(C_6H_4)_x$-SO_3^-, x = 0 to 3. Guanidinium crystallizes with 4-biphenylsulfonate in two polymorphs (by slow evaporation) as determined by IR spectroscopy. Elemental analysis confirms that the two polymorphs have identical chemical compositions and that neither is a solvate. Polymorph I crystallizes as light tan needles from equimolar solutions of guanidine hydrochloride and 4-biphenylsulfonic acid in cosolvent mixtures of methanol with acetone, acetonitrile, or ethyl acetate. Polymorph II, light tan thin squarish plates, is obtained from methanol or methanol/toluene solutions. In some cases both polymorphs were isolated from the same solutions.

Infrared spectra of the two polymorphs are distinct, with major differences occurring in the N-H stretching region ~3400-3100 cm^{-1} and in the N-H bending region ~1700-1600 cm^{-1}. In polymorph I, N-H stretching bands occur at 3404, 3354, 3260, and 3190 cm^{-1} with one N-H bending band at 1652 cm^{-1}. The N-H stretching bands in polymorph II occur at 3469, 3344, 3259 and 3184 cm^{-1} with two N-H bending bands at 1698 and 1656 cm^{-1}. The high wavenumber bands at 3369 and 1698 cm^{-1} in polymorph II are indicative of non-hydrogen-bonded N-H. It is interesting to note that both polymorphs have nearly identical melting points of 274-275 °C (polymorph I) and 273.5-274.5 °C (polymorph II).

The single crystal X-ray structure of polymorph II was solved. The X-ray structural data follows: $C_{13}H_{15}N_3O_3S$, M_r = 293.34, triclinic, $P\bar{1}$ a = 6.213 (4), b = 7.132 (2), c = 15.924 (3) Å, α = 85.63 (2), β = 80.93 (3), γ = 85.19 (4)°, V = 692.9 (9) $Å^3$, Z = 2, D_c = 1.406 g/cm^3, λ(Mo Kα) = 0.71069 Å, μ = 2.32 cm^{-1}, F(000) = 308, T = 297 K, R = 0.040, R_w = 0.048 for 2746 observed reflections. The structure is composed of hydrogen bond ribbons having four of the usual guanidinium-sulfonate hydrogen bonds linked into sheets by one other guanidinium-sulfonate N-H...O hydrogen bond and one guanidinium-sulfonate weak interaction; the sheets pack with a bilayer structure (Figure 1). The hydrogen bond pattern found in polymorph II (Figure 2) differs from the fully hydrogen-bonded pattern found previously in other guanidinium sulfonates in which the ribbons are linked by two hydrogen bonds through translation in two directions, rather than one. These two modes of packing of ribbons are illustrated schematically in Figure 3. Hydrogen bonds in polymorph II range in N...O length from 2.85 to 3.00 Å (average 2.92 Å) with N-H...O angles from 163 to 176° (average 169°). The guanidinium-sulfonate weak interaction has a N...O distance of 3.07 Å and N-H...O angle of 122°.

Preliminary X-ray data for polymorph I follows: $C_{13}H_{15}N_3O_3S$, M_r = 293.34, monoclinic, *C2/m*, a = 32.56 (2), b = 8.161 (8), c = 10.457 (5) Å, β = 99.90 (4)°, V = 2737 (6) Å^3, Z = 8, D_c = 1.423 g/cm^3, λ(Mo Kα) = 0.71069 Å, T = 297 K, R = 0.143, R_w = 0.186 for 1640 observed reflections. Views of crystal packing diagrams (Figure 4) show that the salt has a bilayer structure. Although the structure has not been refined and has a large error at this time (R = 14 %), we are reasonably confident that the hydrogen bond pattern in polymorph I is the usual fully hydrogen-bonded type, as in Figure 1b. IR spectral data supports this conclusion since the N-H stretching bands in polymorph I occur at wavenumbers consistent with hydrogen-bonded N-H. The two hydrogen-bond polymorphs presented here give new insight into the molecular packing modes of guanidinium sulfonates and will be useful in the further studies of these salts.

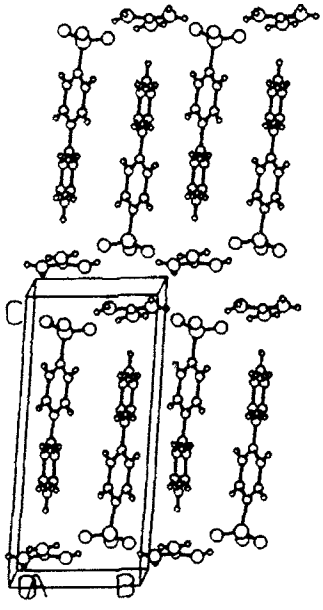


Figure 1. View along the *a*-axis of polymorph II showing the bilayer structure.

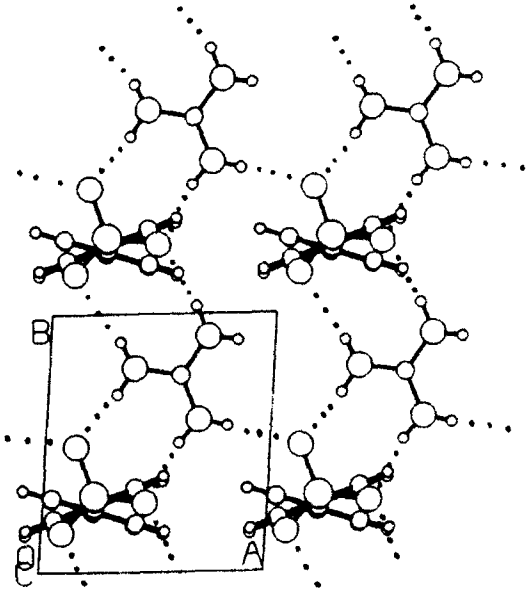


Figure 2. View along the c-axis of polymorph II showing one hydrogen-bonded sheet (hydrogen bonds indicated by dotted lines).

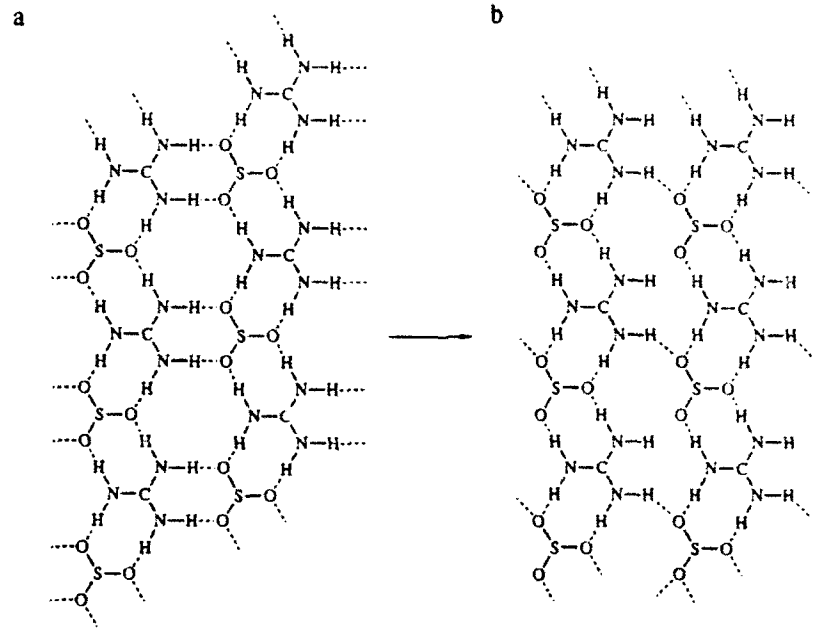


Figure 3. Schematics of two-dimensional hydrogen-bond arrangements in guanidinium sulfonates. (a) Common motif found previously and expected motif for polymorph I. (b) Motif found in polymorph II.

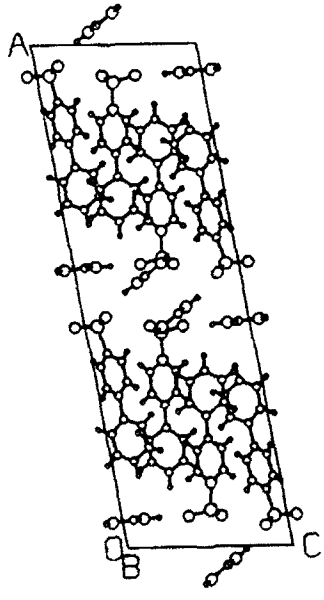


Figure 4. Preliminary view along the *b*-axis of polymorph I. Note that the refinement of the structure is not complete and the guanidinium ions are not in the correct orientation.

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