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Solid-State Structure of a Layered Hydrogen-Bonded Salt: Guanidinium 5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonate Methanol Solvate

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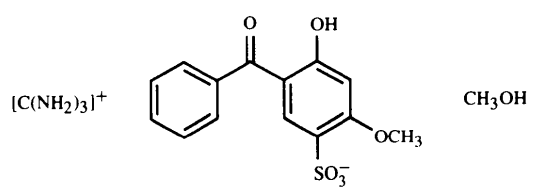
Abstract

Guanidinium 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonate methanol solvate $[C(NH_2)_3^+.(C_{14}H_{11}O_3)SO_3^-.CH_3OH]$ crystallizes into a layered structure containing a two-dimensional hydrogen-bonded network typical of guanidinium alkane- and arenesulfonates. All six guanidinium protons and six sulfonate oxygen lone-pair acceptors participate in hydrogen bonding to form nearly planar pseudohexagonal hydrogen-bonded sheets, which can be viewed as parallel connected hydrogen-bonded ribbons. The 5-benzoyl-4-hydroxy-2-methoxybenzene groups are oriented to the same side of each ribbon, but the orientation of these groups on adjacent ribbons alternates with respect to the hydrogen-bonded sheet. The planar sheets stack with interdigitation of the arene groups, resulting in a structure in which layers of 5-benzoyl-4-hydroxy-2-methoxybenzene groups are separated by ionic hydrogen-bonded sheets. Each methanol molecule forms a hydrogen bond to one of the sulfonate O atoms, resulting in this oxygen forming a total of three hydrogen bonds, and fills void volume between the interdigitated 5-benzoyl-4-hydroxy-2-methoxybenzene groups of neighboring sheets. The benzophenone hydroxyl proton forms an intramolecular hydrogen bond to the carbonyl oxygen.

1. Introduction

Sulisobenzone [also named 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid, benzophenone-4 or Sungard™, Merck Index no. 8963 (Budavari, 1989)] is commonly utilized as an UV screen and as an UV stabilizer in wool, cosmetics, pesticides and lithographic plate coatings (Knox, Griffin & Hakim, 1960; Knox, Guin & Cockerell, 1957). We were interested in the structure of this compound in the context of other experiments ongoing in our laboratory, namely, sulisobenzone adsorption on and intercalation into ordered hydrotalcite clays (Cai, Hillier, Franklin, Nunn & Ward, 1994). Atomic force microscopy (AFM) studies suggested that the adsorption of the sulisobenzone monoanion onto the hexagonally ordered hydrotalcite surface was consistent with (sulfonate)O···H—O(Mg or Al) hydrogen bonding, with threefold sulfonate groups sitting on triads of hydroxyl groups having threefold symmetry. However, the detailed molecular structure of the monoanion could not be discerned directly from the AFM studies. Furthermore, the crystal structure of sulisobenzone has not been reported, presumably because of the difficulty in isolating X-ray quality crystals; indeed, our numerous attempts to grow X-ray quality crystals of sulisobenzone or the sodium salt of the monoanion resulted in only powdery solids. We reported recently a series of guanidinium alkane- and arenesulfonates with the general formula $[C(NH_2)_3]^+[RSO_3]^-$ (Russell, Etter & Ward, 1994*a*,*b*). Structural characterization of these salts revealed unique pseudohexagonal hydrogen-bonded sheets (Fig. 1) formed by hydrogen bonding between the O atoms of the threefold sulfonate ions and the protons of the threefold guanidinium ions, with the *R* groups sandwiched between hydrogen-bonded sheets. The environment of the sulfonate ion in these salts therefore resembled that surmised from spectroscopic and AFM data acquired for the sulisobenzone anion adsorbed on hydrotalcite. This prompted us to prepare the guanidinium salt of the monoanion, which crystallized as the methanol solvate $C(NH_2)_3^+.(C_{14}H_{11}O_3)SO_3^-.CH_3OH$ (I). Interestingly, (I) exhibits the same hydrogen-bonding motif observed in other guanidinium arenesulfonates, even though the sulisobenzone monoanion is substantially larger than the arene residues in these materials. This study illustrates the persistence of the hydrogen-bonded networks in guanidinium sulfonates and provides the first complete structural characterization of the sulisobenzone molecule.



(I)

2. Experimental

Crystals of (I) were obtained as colorless to light yellow (depending upon crystal thickness) laths by slow evaporation of a methanol solution containing 1 equiv. of guanidine carbonate (Sigma) and 2 equiv. of 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid (Pfaltz and Bauer) at room temperature. Details of the X-ray structural determination are given in Table 1.* For the analysis, a crystal was cut to the dimensions $0.6 \times 0.6 \times 0.12$ mm. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods with *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984), utilizing the *TEXSAN* system (Molecular Structure Corporation, 1985). The structure was refined in both polarities. For the enantiomer reported (right-handed configuration with respect to the 2_1 screw axis along +c), $R = 0.046$ and $wR = 0.054$; for the opposite enantiomer, $R = 0.047$ and $wR = 0.055$. Molecular graphics were created with *PLUTO* (Motherwell & Clegg, 1976) and *ORTEP* (Johnson, 1965) within the *TEXSAN* program.

Other characterizations: DSC (with concurrent visual observation): 398–403 (br, endotherm, clear crystal turns opaque, loss of MeOH), 507–509 (endotherm, melt), 509–514 K (exotherm, solidification to an unidentified phase); IR (Nujol): [ν(O—H) 3512], [ν(N—H) 3373, 3330, 3255, 3199], [δ(NH) 1675], [ν(C═O) 1627], 1600, 1578, 1490, 1463 (Nujol), 1378 (Nujol), 1345, 1266, [ν(S—O), (C—O) 1219, 1197 (sh), 1187, 1171, 1164, 1084, 1030, 1000], 942, 934, 917, 882, 843, 820, 787, 766, 741, 724, 695, 685, 668, 650, 612 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.92 (*s*, 1 H, 6-*H*, *ortho* to SO_3^-),

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares planes data have been deposited with the IUCr (Reference: BK0027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

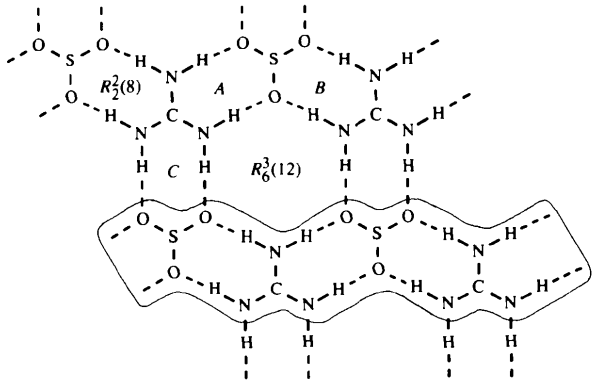


Fig. 1. Schematic representation of the hexagonal hydrogen-bonded sheet motif typical of guanidinium sulfonates. Hydrogen-bonded cyclic dimers *A* and *B* of the graph set motif form ribbons parallel to one unit-cell direction (a single ribbon is outlined). The ribbons are linked by dimer *C* interactions and rings.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$[C(NH_2)_3]^+.C_{14}H_{11}O_3S^-.CH_4O$
Chemical formula weight	399.42
Cell setting	Orthorhombic
Space group	$Pna2_1$
a (Å)	18.640 (5)
b (Å)	13.088 (8)
c (Å)	7.502 (4)
V (Å^3)	1830 (2)
Z	4
D_x (Mg m^{-3})	1.449
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	23
θ range (°)	11–22
$F(000)$	840
μ (mm^{-1})	0.211
Temperature (K)	297
Crystal form	Laths
Crystal size (mm)	0.60 × 0.60 × 0.12
Crystal color	Colorless
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω scans
Absorption correction	Refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min}	0.83
T_{max}	1.14
No. of measured reflections	3078
No. of independent reflections	2509
No. of observed reflections	2454
Criterion for observed reflections	$I > 2.0\sigma(I)$
R_{int}	0.096
θ_{max} (°)	27.95
Range of h, k, l	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 17$ $0 \rightarrow l \rightarrow 24$
No. of standard reflections	3
Frequency of standard reflections	60
Refinement	
Refinement on	F
R	0.046
wR	0.054
S	1.20
No. of reflections used in refinement	2454
No. of parameters used	275
H-atom treatment	Guanidinium and methanol hydroxyl H located on difference map; other H placed in idealized positions
Weighting scheme	$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$	0.03
$\Delta\rho_{max}$ (e Å^{-3})	0.25
$\Delta\rho_{min}$ (e Å^{-3})	−0.35
Extinction method	None
Source of atomic scattering factors	*International Tables for X-ray Crystaloography* (1974, Vol. IV)

7.60 (*m*, 5 H, H on unsubstituted ring), 6.94 (*s*, 6 H, $[C(NH_2)_3]^+$), 6.59 (*s*, 1 H, 3-*H*, *meta* to SO_3^-), 4.09 (*m*, 1 H, CH_3OH, split in DMSO), 3.85 (*s*, 3 H, —OCH_3), 3.17 (*d*, 3 H, CH_3OH, split in DMSO); SHG $\sim\frac{1}{8}\times$ urea.

3. Results and discussion

3.1. *Molecular structure*

The title compound (I) crystallizes in space group $Pna2_1$, with one ion pair and one methanol molecule

in the asymmetric unit. Atomic coordinates are listed in Table 2 and an *ORTEP* (Johnson, 1965) diagram with labeling scheme is shown in Fig. 2. Selected intramolecular bond geometries are given in Table 3. The guanidinium ion geometries are similar to those observed (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) and calculated (Gobbi & Frenking, 1993) for the unsubstituted guanidinium ion. The S—O bond lengths and angles in (I) vary slightly. This behavior differs from that observed generally for sulfonate groups, in which S—O bond lengths and O—S—O bond angles are usually equivalent. The geometries of the benzophenone moiety compare well with those found for the related, unsulfonated analogs oxybenzone (2-hydroxy-4-methoxybenzophenone; Liebich & Parthe, 1974), 2-hydroxy-4-methoxy-4′-chlorobenzophenone (Liebich, 1976), cudranone [2,6,3′-trihydroxy-4-methoxy-2′-(3-methyl-2-butenyl)benzophenone (Otterson, Vance, Doorenbos, Chang & El-Feraly, 1977)] and benzophenone (Fleischer, Sung & Hawkinson, 1968; Lobanova, 1969). The phenyl rings in the guanidinium salt are slightly closer to coplanarity, with a dihedral angle between aryl ring planes of 43°, compared with 49, 50, 77 and 56° for the aforementioned analogs, respectively. Torsion angles of the rings with respect to the carbonyl are 5.0 (6)° for the substituted ring (O5—C18—C13—C14*A*) and 39.2 (6)° for the unsubstituted ring (O5—C18—C19—C24). An intramolecular O—H···O hydrogen bond ($d_{O\cdots O}$ = 2.56 Å, $\theta_{O-H\cdots O}$ = 151°) of graph set motif $S(6)$ (intramolecular ≡ Self hydrogen-bonded six-membered ring; for a discussion of graph set analysis, see Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995) is formed between the proximal hydroxyl and carbonyl groups, as is commonly observed for β-hydroxy carbonyl compounds. The methoxyl methyl group is oriented away from the sulfonate group so that the sulfonate group is sterically accessible for hydrogen bonding with guanidinium and methanol donors.

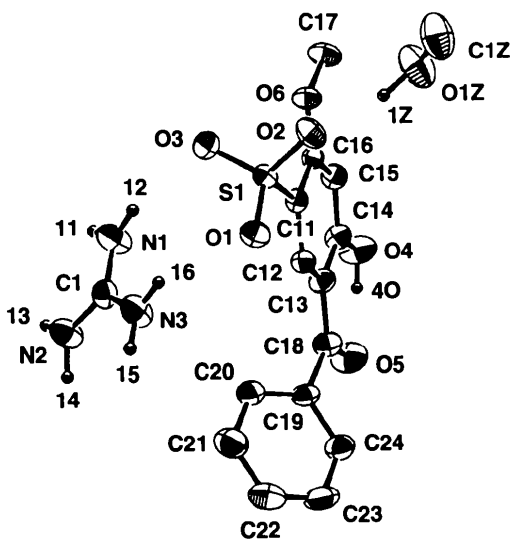


Fig. 2. *ORTEP* (Johnson, 1965) view (50% probability ellipsoids) of the asymmetric unit showing the atomic labeling scheme. Guanidinium and hydroxyl H atoms were isotropically refined (H atoms are labeled by number only); other H atoms are in idealized positions and are omitted.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
S1	0.30198 (4)	0.23973 (5)	3/4	2.02 (2)
O1	0.2791 (1)	0.3457 (1)	0.7424 (5)	2.78 (8)
O2	0.2975 (1)	0.1890 (2)	0.5756 (4)	3.0 (1)
O3	0.2644 (1)	0.1822 (2)	0.8881 (4)	2.8 (1)
O4	0.6030 (1)	0.2417 (3)	0.9868 (6)	4.1 (1)
O5	0.5954 (2)	0.4364 (3)	1.0125 (6)	4.2 (2)
O6	0.3977 (1)	0.0646 (2)	0.7809 (4)	2.6 (1)
C11	0.3928 (2)	0.2421 (2)	0.8138 (5)	2.0 (1)
C12	0.4256 (2)	0.3340 (2)	0.8559 (5)	2.2 (1)
C13	0.4960 (2)	0.3387 (3)	0.9218 (6)	2.6 (1)
C14	0.5347 (2)	0.2459 (3)	0.9326 (5)	2.7 (1)
C15	0.5032 (2)	0.1532 (2)	0.8850 (5)	2.6 (1)
C16	0.4326 (2)	0.1509 (2)	0.8285 (5)	2.1 (1)
C17	0.4366 (2)	−0.0295 (3)	0.7857 (6)	3.3 (2)
C18	0.5309 (2)	0.4348 (3)	0.9723 (6)	2.9 (1)
C19	0.4901 (2)	0.5327 (3)	0.9790 (6)	2.7 (1)
C20	0.4209 (2)	0.5407 (3)	1.0469 (6)	3.1 (2)
C21	0.3873 (2)	0.6346 (4)	1.0536 (8)	4.0 (2)
C22	0.4208 (3)	0.7209 (3)	0.9895 (9)	4.4 (2)
C23	0.4900 (3)	0.7141 (3)	0.9243 (7)	4.1 (2)
C24	0.5247 (2)	0.6210 (3)	0.9202 (6)	3.3 (1)
H40	0.615 (3)	0.305 (4)	1.013 (8)	4 (1)
H1	0.4058	−0.0841	0.7521	4.0
H2	0.4759	−0.0260	0.7056	4.0
H3	0.4539	−0.0411	0.9033	4.0
H4	0.5302	0.0917	0.8917	3.1
H5	0.3969	0.4814	1.0886	3.7
H6	0.3405	0.6397	1.1034	4.9
H7	0.3963	0.7846	0.9897	5.3
H8	0.5138	0.7736	0.8825	4.9
H9	0.5725	0.6172	0.8767	3.9
H10	0.3996	0.3957	0.8396	2.7
N1	0.2663 (2)	0.3018 (3)	1.2396 (7)	3.9 (1)
N2	0.2549 (2)	0.4519 (3)	1.3946 (6)	3.6 (1)
N3	0.2392 (2)	0.4498 (3)	1.0929 (6)	3.6 (2)
C1	0.2534 (2)	0.4009 (2)	1.2445 (7)	2.7 (1)
H11	0.274 (3)	0.274 (4)	1.337 (8)	4 (1)
H12	0.255 (4)	0.266 (5)	1.14 (1)	6 (2)
H13	0.269 (2)	0.422 (3)	1.507 (6)	1.9 (8)
H14	0.260 (3)	0.523 (4)	1.40 (1)	5 (1)
H15	0.225 (3)	0.517 (4)	1.085 (8)	4 (1)
H16	0.234 (2)	0.414 (3)	1.000 (7)	3 (1)
O1Z	0.3948 (2)	0.0641 (4)	0.3800 (6)	5.3 (2)
C1Z	0.3510 (3)	0.0522 (5)	0.2314 (8)	5.4 (2)
H1Z	0.371 (3)	0.113 (5)	0.45 (1)	7 (2)
H2Z	0.3468	0.1161	0.1708	6.4
H3Z	0.3712	0.0032	0.1536	6.4
H4Z	0.3048	0.0305	0.2686	6.4

3.2. *Crystal packing*

The solid-state packing in (I) is governed by ionic hydrogen bonds between guanidinium and sulfonate groups, van der Waals interactions between the aryl rings and close-packing of methanol molecules in voids between hydrogen-bonded molecular layers. A molecu-

Table 3. *Selected geometric parameters (Å, °)*

S1—O1	1.453 (2)	N3—C1	1.331 (5)
S1—O2	1.470 (3)	O1Z—C1Z	1.390 (7)
S1—O3	1.460 (3)	O4—H40	0.88 (5)
S1—C11	1.760 (3)	C12—H10	0.950
O4—C14	1.337 (4)	C15—H4	0.950
O5—C18	1.239 (5)	C17—H1	0.951
O6—C16	1.352 (4)	C17—H2	0.949
O6—C17	1.430 (4)	C17—H3	0.951
C11—C12	1.385 (4)	C20—H5	0.950
C11—C16	1.409 (4)	C21—H6	0.951
C12—C13	1.404 (4)	C22—H7	0.951
C13—C14	1.415 (4)	C23—H8	0.950
C13—C18	1.466 (5)	C24—H9	0.949
C14—C15	1.395 (5)	N1—H11	0.83 (6)
C15—C16	1.384 (4)	N1—H12	0.87 (7)
C18—C19	1.491 (5)	N2—H13	0.96 (4)
C19—C20	1.391 (5)	N2—H14	0.93 (5)
C19—C24	1.396 (5)	N3—H15	0.92 (5)
C20—C21	1.379 (6)	N3—H16	0.85 (5)
C21—C22	1.378 (7)	O1Z—H1Z	0.96 (7)
C22—C23	1.382 (8)	C1Z—H2Z	0.954
C23—C24	1.380 (6)	C1Z—H3Z	0.947
N1—C1	1.319 (4)	C1Z—H4Z	0.949
N2—C1	1.310 (6)		
O1—S1—O2	112.3 (2)	C11—C12—H10	119.04
O1—S1—O3	112.3 (2)	C13—C12—H10	118.94
O1—S1—C11	106.0 (1)	C14—C15—H4	120.12
O2—S1—O3	111.8 (2)	C16—C15—H4	120.02
O2—S1—C11	107.7 (2)	O6—C17—H1	109.48
O3—S1—C11	106.1 (2)	O6—C17—H2	109.52
C16—O6—C17	118.0 (3)	O6—C17—H3	109.44
S1—C11—C12	120.1 (2)	H1—C17—H2	109.53
S1—C11—C16	120.8 (2)	H1—C17—H3	109.34
C12—C11—C16	119.1 (3)	H2—C17—H3	109.52
C11—C12—C13	122.0 (3)	C19—C20—H5	119.68
C12—C13—C14	117.4 (3)	C21—C20—H5	120.18
C12—C13—C18	122.9 (3)	C20—C21—H6	119.55
C14—C13—C18	119.6 (3)	C22—C21—H6	119.67
O4—C14—C13	122.6 (3)	C21—C22—H7	120.12
O4—C14—C15	116.3 (3)	C23—C22—H7	120.32
C13—C14—C15	121.1 (3)	C22—C23—H8	120.06
C14—C15—C16	119.9 (3)	C24—C23—H8	119.76
O6—C16—C11	115.7 (3)	C19—C24—H9	119.85
O6—C16—C15	123.8 (3)	C23—C24—H9	119.63
C11—C16—C15	120.4 (3)	C1—N1—H11	116 (4)
O5—C18—C13	120.6 (3)	C1—N1—H12	120 (5)
O5—C18—C19	118.1 (3)	H11—N1—H12	121 (5)
C13—C18—C19	121.3 (3)	C1—N2—H13	124 (2)
C18—C19—C20	123.4 (3)	C1—N2—H14	123 (4)
C18—C19—C24	117.8 (3)	H13—N2—H14	109 (5)
C20—C19—C24	118.7 (4)	C1—N3—H15	125 (4)
C19—C20—C21	120.1 (4)	C1—N3—H16	117 (3)
C20—C21—C22	120.8 (4)	H15—N3—H16	117 (5)
C21—C22—C23	119.6 (4)	C1Z—O1Z—H1Z	105 (4)
C22—C23—C24	120.2 (4)	O1Z—C1Z—H2Z	109.38
C19—C24—C23	120.5 (4)	O1Z—C1Z—H3Z	109.65
N1—C1—N2	121.4 (4)	O1Z—C1Z—H4Z	109.32
N1—C1—N3	119.0 (4)	H2Z—C1Z—H3Z	109.40
N2—C1—N3	119.6 (3)	H2Z—C1Z—H4Z	109.23
C14—O4—H40	105 (3)	H3Z—C1Z—H4Z	109.84

Table 4. *Hydrogen-bond geometries* (Å, °)

Dimer*	*D*—H···O	*D*—H	*D*···O	H···O	*D*—H···O
A	N1—H12···O3^{i}	0.87 (7)	3.067 (6)	2.22 (7)	161.47
A	N3—H16···O1^{i}	0.85 (5)	3.053 (5)	2.29 (5)	150.04
B	N1—H11···O2^{ii}	0.83 (6)	2.979 (5)	2.15 (6)	174.51
B	N2—H13···O1^{ii}	0.96 (4)	2.991 (6)	2.04 (4)	168.50
C	N2—H14···O3^{iii}	0.93 (5)	3.036 (5)	2.14 (5)	161.36
C	N3—H15···O2^{iii}	0.92 (5)	3.208 (5)	2.29 (5)	173.39
	O4—H40···O5^{i}	0.88 (5)	2.559 (5)	1.754	150.88
	O1Z—H1Z···O2^{i}	0.96 (7)	2.848 (5)	1.92 (7)	162.74

Symmetry codes: (i) x, y, z; (ii) $x, y, z+1$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$. *See Fig. 2 for dimer labeling. Dimers *A* and *B* comprise hydrogen-bonded ribbons parallel to the *z* axis. Linkage into sheets is through dimer *C* interactions along the *y* axis.

lar packing diagram illustrating the hydrogen-bonding interactions is depicted in Fig. 3 and hydrogen bond geometries are given in Table 4. Each individual pair of N—H···O interactions can be characterized as a cyclic dimer formed *via* two amino protons on two N atoms of a single guanidinium ion and two lone-electron pairs on two O atoms of a sulfonate ion. This ring motif has graph set notation $R_2^2(8)$ (eight-membered Ring involving two acceptors and two donors). The ions in (I) self-assemble into an almost planar two-dimensional guanidinium sulfonate hydrogen-bonded network (Fig. 1), in which guanidinium-sulfonate hydrogen-bonded dimers (*A* and *B*) comprise translationally-related ribbons parallel to the *z* axis. Hydrogen bonding *via* $R_2^2(8)$ dimers (labeled *C*) and $R_6^3(13)$ rings links *n*-glide-related ribbons along the *y* direction, generating hydrogen-bonded (100) sheets.

The six unique guanidinium sulfonate hydrogen bonds in (I) range in $d_{N\cdots O}$ length from 2.98 to 3.21 Å (av. 3.06) and $\theta_{N-H\cdots O}$ angle from 150.0 to 174.5° (av. 164.9). These hydrogen bonds are slightly longer than those found in other guanidinium sulfonates, which ranged from 2.84 to 3.06 Å (av. 2.93) for 14 alkane- and arenesulfonates (Russell, Etter & Ward, 1994*a*,*b*). The lengths are also longer than the average $d_{N\cdots O}$ of 2.946 Å reported for N—H···O(sulfonate) hydrogen bonds in a recent database survey (Pirard, Baudoux & Durant, 1995). The survey also reported an average $\theta_{N-H\cdots O}$ of 150.7°, similar to the hydrogen-bond angles

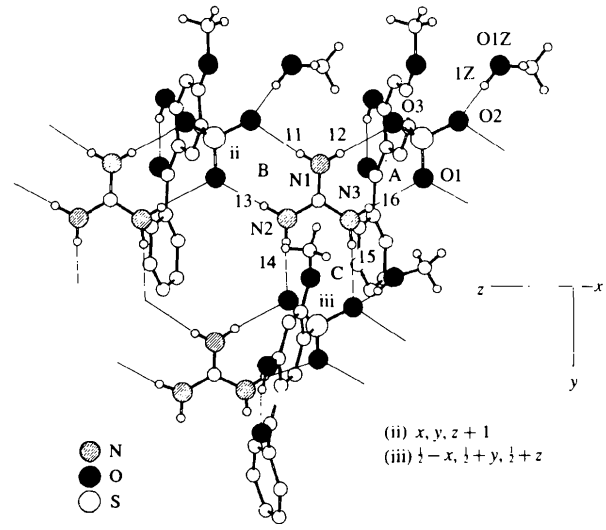


Fig. 3. Environment around the guanidinium ion [projection onto (1̄00)] showing the hydrogen-bonded sheet motif and atomic labeling of relevant atoms (H atoms are labeled by number only). Hydrogen bonds are indicated by thin lines. Hydrogen-bonded cyclic dimers *A* and *B* form ribbons parallel to **z**. Neighboring almost coplanar ribbons are linked by dimer *C* interactions.

observed here. The N—H···O interaction of length 3.21 Å (N3—H15···O2) in our compound is longer than generally accepted for a hydrogen bond [$d_{N\cdots O}$ = 3.07 Å = sum of van der Waals radii for N and O (Bondi, 1964)]. However, based on the almost linear arrangement ($\theta_{N—H\cdots O}$ = 173°), the directionality of the interaction cannot be disputed. In any case, the topology of the guanidinium sulfonate sheet is identical to that found in other guanidinium sulfonates, supporting our contention that the N3—H15···O2 interaction is a hydrogen bond. In addition to participating in two separate guanidinium–sulfonate dimer interactions, the sulfonate oxygen O2 also acts as a hydrogen-bond acceptor for the methanol proton, resulting in this oxygen accepting a total of three hydrogen bonds. The unusual geometry of the sulfonate oxygen O2 may be a result of a balance of crystal packing forces involving multiple hydrogen bonds and close-packing tendencies. Of the other potential hydrogen-bonding sites, the poorly accepting methoxyl O atom does not participate in hydrogen bonding and the hydroxyl proton is involved in intramolecular hydrogen bonding to the carboxyl acceptor.

The hydrogen-bonded sheets assemble into a layered structure, with the formation of hydrophobic and polar regions (Figs. 4 and 5). The aryl fragments of the sulisobenzone anions are oriented to the same side of each ribbon, but their orientation on adjacent ribbons alternates with respect to the hydrogen-bonded sheet. This arrangement was previously referred to as a 'single-layer' motif (Russell, Etter & Ward, 1994*a*). The single-layer motif is expected for (I) based on steric considerations. Crystallization into bilayer (all *R* groups oriented to one side of the hydrogen-bonding plane) *versus* single layer (*R* groups alternate orientation across the hydrogen-bonding plane) motifs can be explained by the size (*i.e.* width) of the *R* group projected along the threefold axis of the sulfonate group. The 7 Å width of the sulisobenzone (not including the methoxyl group or ring hydrogens, $d_{C23\cdots C15}$ = 7.35 Å) exceeds the steric limit for formation of the bilayer structure, which is defined by the center-to-center distance between nearest sulfonate ions (4.4 Å). The interribbon dihedral angle, θ_{IR}, a measure of the degree of puckering of the hydrogen-bonded sheet, is 165°, comparable with that observed for other guanidinium arenesulfonates with bilayer structures (typically, 150–165°). However, the near planarity of the hydrogen-bonded sheet in (I) contrasts single-layer motifs in previously reported guanidinium sulfonates. For example, severely puckered hydrogen-bonded sheets were observed in guanidinium (1*S*)-(+)-10-camphorsulfonate and guanidinium 1-naphthalenesulfonate, with θ_{IR} values of 122 and 77°, respectively. The puckering of hydrogen-bonded sheets in those structures was attributed to the tendency to maximize favorable van der Waals contacts between the sulfonate *R* groups and attain close packing. Significant puckering of the sheets in (I) probably does not occur because the methanol molecules fill the empty space in the interlayer region between the aryl groups of the sulfonate ions directly below the voids of the hexagonal hydrogen-bonded net (see Figs. 1 and 3). The resulting density increase in the interlayer region reduces the tendency for the sheets to pucker. The packing coefficient of the methanol solvate (I) is 0.71, with a density of 1.45 g cm^{-3}; for comparison, the same structure with the methanol molecules removed has a packing coefficient of 0.63 with a density of 1.33 g cm^{-3} [packing coefficients obtained from packing volumes calculated with *Cerius*2 (Molecular Simulations, Inc. 1995)]. Organic crystal structures are not generally observed with packing coefficients below ~0.65 (Kitaigorodsky, 1973). Crystals of (I) are stable to methanol loss for at least several weeks at room temperature. Differential scanning calorimetry indicated methanol loss at $T \sim 398$ K, significantly higher than the boiling point of methanol (338 K). This suggests that methanol incorporation and retention is favored by hydrogen bonding of the methanol proton to the sulfonate O atom.

Compound (I) exhibits trace second-harmonic generation as a result of its crystallization into the noncentrosymmetric space group $Pna2_1$. Our previous studies

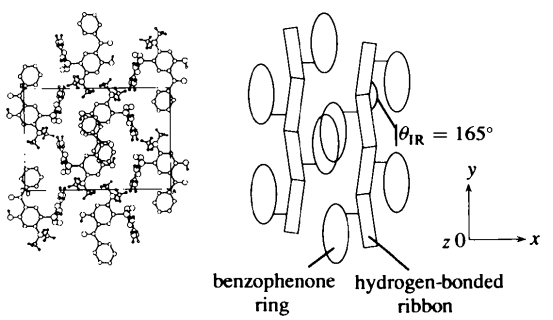


Fig. 4. Crystal-packing diagram [projection onto (001)] and corresponding scheme, illustrating the single layer motif of (I). Note that hydrogen-bonded ribbons project normal to the page and that methanol molecules are omitted from the scheme.

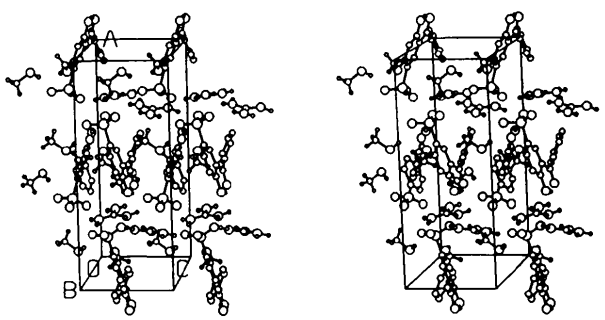


Fig. 5. Stereoview approximately along the *y* axis, showing the layering structure, partitioning into hydrophobic and polar regions, and the space-filling nature of the methanol molecules. Hydrogen-bonded layers (two shown) are oriented horizontally at $x = \frac{1}{4}, \frac{3}{4}$ in the cell.

indicated that guanidinium alkane- and arenesulfonates crystallized into centrosymmetric space groups unless competitive hydrogen bonding by sulfonate substituents significantly perturbed the sheet motif or a chiral sulfonate was used. The unsymmetrically substituted benzophenone molecule may influence the packing into a noncentrosymmetric phase.

We surmise that our successful isolation of X-ray quality crystals of sulisobenzone as its guanidinium salt (I) resulted from the stability of the guanidinium sulfonate extensively hydrogen-bonded network. Thus, preparation of guanidinium salts may be a useful technique for the growth of otherwise elusive sulfonate crystals. The structure of (I) is consistent with the results of our previous studies of adsorption of sulisobenzone anions on hydrotalcite, in which the sulfonate group interacts with a triad of hydroxyl protons on the hydrotalcite surface.

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