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The Origin of Bulk Polarity in Hydrogensulfate Salts

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The crystal packing motifs exhibited by hydrogensulfate salts, including 10 new organic cation salts, are analyzed in the context of understanding the criteria that control bulk polarity in the absence of chiral moieties. Fortyfive hydrogensulfate salts were analyzed, 27 crystallize *via* head-to-tail strand motifs that are conducive to the presence of bulk polarity, 16 crystallize *via* packing of dimer motifs and 2 exhibit cocrystallization of both strand and dimer motifs. The majority of the strand motifs randomly aggregate *via* one of the expected crystallographic operations: translation, glide or screw. However, only 8 compounds crystallize in non-centrosymmetric space groups. The most desirable aggregate from the perspective of maximizing bulk polarity, the translation aggregate, was observed in 9 compounds. We discuss our observations in the broader context with particular emphasis on the development of strategies for crystal engineering of polar solids.

INTRODUCTION

The emerging discipline of crystal engineering has important implications for materials science since it implies that solids can be designed for specific topological features and, ultimately, bulk physical properties. Such an idea would have been unthinkable, especially for organic solids, as recently as a decade ago.[1] However, recent advances in the theoretical and experimental understanding of molecular recognition have afforded chemists greater ability to impart control over 1-D[2], 2-D[3] or, ultimately, 3-D[4] aggregates. One can therefore assume that molecular recognition is the guiding force for crystal packing. In such a context, hydrogen bonding represents a primary "synthetic vector"[5] for crystal engineers, a tool which, if sufficiently understood, can be used to design and predict the structures of supramolecular aggregates.[6] This contribution concerns the nature of hydrogen bonding in hydrogensulfate salts and bulk polarity, a prerequisite for a number of important bulk physical properties ranging from piezoelectricity to second harmonic generation.[7]

Strategies for controlling bulk polarity in the absence of a single enantiomer[3c,3d,3k,4i,8] have tended to rest upon forming aggregates that have parallel alignment of dipoles. The "head-to-tail" strand motifs exhibited by carboxylic acids[9] (Figure 1a), nitroanilines[2e,f] (Figure 1b) and vanillin-I[10] illustrate well how achiral molecules can crystallize in polar space groups. Whether adjacent strands align anti-parallel or parallel determines if bulk polarity is present since all

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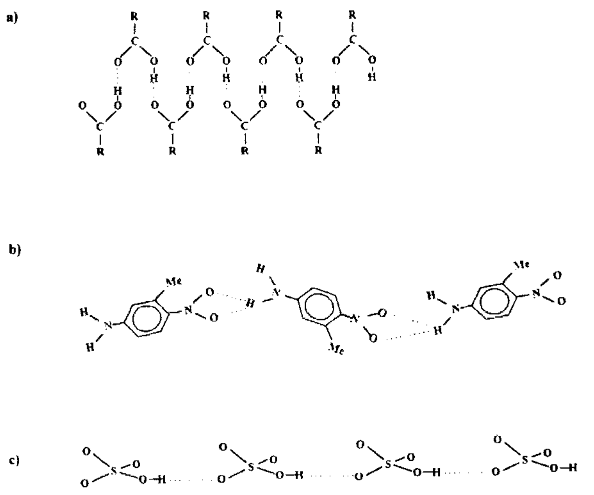

FIGURE 1 Schematic representation of the 1-D polar aggregates that can result from self-assembly of carboxylic acids **(a)**, nitroanilines **(b)** and the hydrogensulfate anion **(c)**.

three form strands that are inherently polar. In the case of carboxylic acids that form strand aggregates it has been noted that there is effectively a random chance of the crystal being polar.[2d] This might not seem like a significant advance in our ability to control bulk polarity until one considers that only *ca.* 25 percent of organic compounds in the Cambridge Structural Database crystallize in polar space groups, including pure enantiomers.[11] The hydrogensulfate anion represents another species that has inherent ability to self-assemble into polar strands (Figure 1c). Indeed, several inorganic cation hydrogensulfate salts are known to be ferroelectric[12] and organic cation hydrogensulfate salts have been studied for similar reasons.[2g] In this contribution, we present a detailed analysis of the crystal packing in all previously reported simple hydrogensulfate salts and 10 new organic cation salts.

RESULTS AND DISCUSSION

The primary purpose of this study is to aid our understanding of how directional intermolecular or interionic interactions can be exploited to induce bulk polarity in crystals in the absence of chiral residues. Searches of the Cambridge Structural Database[11a], the CISTI database[13], and the synthesis and x-ray structural characterization of 10 new salts provided our sources of data. We chose to focus primarily upon organic cations, but also included relevant inorganic and organometallic cations. Fortyfive compounds in which the anions self-assemble were analyzed, excluding several compounds in which the anions do not self-assemble.

The hydrogensulfate anion may satisfy its strong hydrogen bonding capabilities (Figure 2) by forming either infinite strands or dimers (Figure 3). There are 3 likely strand aggregates based upon common crystallographic symmetry operations: translation (**A**), glide (**B**) and screw (**C**). **A–C** are inherently polar, however, in order for this polarity to extend to the bulk solid, parallel alignment of adjacent strands is required. One might expect this to be the likely origin of bulk polarity in the 8 polar structures discussed herein, however, this is not necessarily the case since polarity can also be achieved by parallel alignment of cations. Of the 45 salts investigated, the anions of 27 self-assemble to afford only strands, 16 yield only dimers and 2 contain both dimers and strands. This distribution indi-

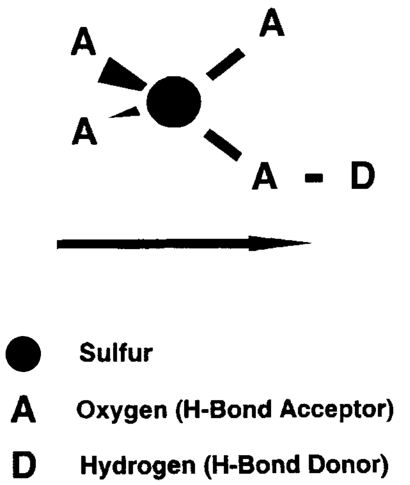

FIGURE 2 Schematic representation of the hydrogensulfate anion, a "synthetic vector" with one hydrogen bond donor and three hydrogen bond acceptors.

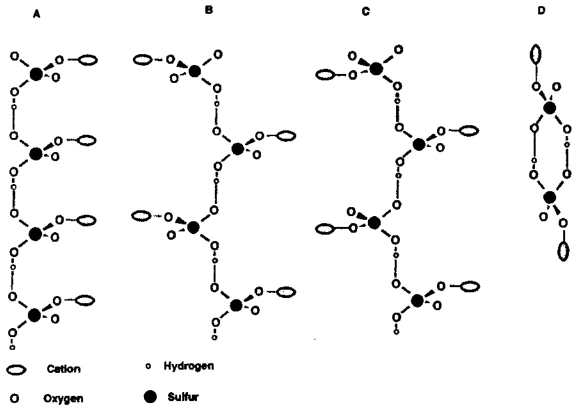

FIGURE 3 Schematic representation of the 4 motifs likely to result from self-assembly of the hydrogensulfate anion: translation (**A**), glide (**B**), screw (**C**) and inversion (**D**) aggregates.

cates that the hydrogensulfate anion is indeed an appropriate component for incorporation into or even design of polar solids. An approximately random distribution of strand aggregates occurs: 11 translation aggregates, 12 glide aggregates (two of which cocrystallize with dimers and one of which cocrystallizes with a screw aggregate) and 6 screw aggregates (one of which coexists with a glide aggregate). A general discussion of these observations is followed by a more detailed discussion of the 10 new organic cation salts.

Translation Aggregates: Table I summarizes the 11 salts which crystallize as translation or type A aggregates: [pyridinium][HSO_4][14] **(A1)**, [2,6-lutidinium][HSO_4] **(A2)**, [isoquinolinium][HSO_4] **(A3)**, [5,6,7,8-tetrahydroisoquinolinium][HSO_4] **(A4)**, [cephapyrine][HSO_4][15] **(A5)**, [tetramethylammonium][HSO_4][16] **(A6)**, [CH_3COOH_2] [HSO_4][17] **(A7)**, [1-((4-(3-chlorophenylamino)-3-pyridyl)sulfonyl)-3-ethyl-1-methylurea][HSO_4][18] **(A8)**, [2,4-dimethyl-l-(1'-hydroxyethylamide-)-benzene][HSO_4][19] **(A9)**, $RbHSO_4$[20] **(A10)**, and [NH_4][HSO_4][21] **(A11)**. Nine of these compounds generate simple translations, whereas two, **A2** and **A6**, contain two independent pairs of ions and are generated by translation of $[HSO_4]_2[cat]_2$ units. **A6** crystallizes in a polar space group and **A2** is discussed in a subsequent section.

Three of the type **A** aggregates crystallize in polar space groups: **A3**, **A4** and **A5**. **A3** and **A4** are polar despite anti-parallel arrangement of adjacent anionic strands. Full details of the structures of **A3** and **A4** are presented subsequently. **A5** is the only example of the most desirable motif: a type **A** aggregate in which adjacent strands of anions align parallel to one another. This arrangement would intuitively be expected to generate the highest degree of polarity because the cations also necessarily align. Interestingly, this salt is also the only one in this study with a chiral cation.[22] Of course, crystals of pure enantiomers must crystallize in polar space groups, however, this does imply that they should also adopt translation aggregates.

Glide Aggregates: The 12 glide or type **B** aggregates are summarized in Table II: [2,4,6-collidinium][HSO_4] **(B1)**, [2,4-lutidinium][HSO_4] **(B2)**, [4,4'-bipyridinium][HSO_4] **(B3)**, [2-aminobenzimidazolium][HSO_4] **(B4)**, [5,7-diphenyl-1,3-diazatricyclo[3.3.1.1.]decan-6-one][HSO_4][23] **(B5)**, [phenanthrolinium][HSO_4][24] **(B6)**, [hydroxytriphenylarsonium][HSO_4][25] **(B7)**, [benzotriazolium][HSO_4][26] **(B8)**, [hydronium][HSO_4][27] **(B9)**, [2-amino-5-nitropyridinium][HSO_4][28] **(B10)**, a cocrystal of glide and screw aggregates, $KHSO_4$[12c] **(B11)** and $[K_{0.55}Rb_{0.45}]$[HSO_4][28] **(B12)**, both of which are cocrystals of glide aggregates and dimers. That cocrystallization of different aggregate types can occur is an indication that there is little energy difference between the four classes and that polymorphism might therefore be prevalent in hydrogensulfate salts. Three of the 9 type **B** aggregates crystallize in polar space groups: **B1**, **B2** and **B5**. The polarity of **B1** and **B2** is a consequence of parallel alignment of cations since the anionic strands are anti-parallel. However, adjacent strands in **B5** align parallel to one another, thereby affording a favourable situation from the perspective of bulk polarity. The cation in **B5**, 5,7-Diphenyl-1,3-diazatricyclo-[3.3.1]decan-6-one, is somewhat bulky, but it is not clear if this is an important factor.

TABLE I Summary of the Type A (Translation Aggregate) Salts

Cation Code[a]	Compound Type[b]	Space Group	Polar	Interionic Distances (Å)	Source[c]
A1 pyridinium	org	P1	N	S-S: 4.664 O-O: 2.570 N-O: 2.921	Ref. 14
A2[d] 2.6-lutidinium	org	P1	N	S-S: 4.795(3), 4.835(3) O-O: 2.660(5), 2.566(5) N-O: 2.845(5), 2.934(5), 2.893(5), 2.906(5)	This study
A3 isoquinolinium	org	$P2_1$	Y	S-S: 4.588(3) O-O: 2.487(7) N-O: 2.862(12)	This study
A4 5,6,7,8-tetrahydro isoquinolinium	org	$P2_1$	Y	S-S: 4.6372(22) O-O: 2.505(5) N-O: 2.859(7)	This study
A5 cephapyrine	org	P1	Y	S-S: 4.632 O-O: 2.615 N-O: 3.231	CEPHAP
A6[d] $[N(CH_3)_4]^+$	org	$P2_1$	Y	S-S: 4.769, 4.802 O-O: 2.553, 2.515 and S-S: 4.759, 4.813 O-O: 2.568, 2.509	JITNOP02
A7 $[CH_3COOH_2]^+$	org	$P2_1/c$	N	S-S: 4.529 O-O: 2.567 O-O[e]: 2.513	ACASUL
A8 $[1-(4-(3-chlorophenylamino)-3-pyridyl)sulfonyl)-3-ethyl-1-methylurea]^+$	org	$P\bar{1}$	N	S-S: 4.553 O-O: 2.659 N-O: 3.080	CPYSUR
A9 [2,4-dimethyl-1-(1'-hydroxy ethylamide)-benzene]	org	$P2_1/c$	N	S-S: 4.690 O-O: 2.605 O-O: 2.516[e] N-O: 2.803	TAFBOR
A10 Rb^+	inorg	$P2_1/c$	N	S-S: 4.618 O-O: 2.531, 2.615	Ref. 20
A11 $[NH_4]^+$	inorg	$B2_1/a$	N	S-S: 4.600 O-O: 2.514, 2.598 N-O[f]:	Ref. 21

a: Cation identity based upon name in CSD, if appropriate; b: org = organic cation, inorg = inorganic cation, c: 6-letter codes are those of the Cambridge Structural Database; d: Translation of $(cat)_2(HSO_4)_2$ unit e: O-O contact is between cation and anion; f: 19 N-O contacts from 2.921 to 3.254Å are reported.

Screw Aggregates: The 6 screw or type **C** aggregates are summarized in Table III: $[3,5\text{-diphenyl-}1,2\text{-dithiolium}][HSO_4]$[29] **(C1)**, [4-hydroxypyridinium] **(C2)**, $[4,9\text{-dimethoxy-}7\text{-methyl-}5H\text{-furo}(3,2\text{-g})(1)\text{benzopyran-}5\text{-one}][HSO_4]$[30] **(C3)**, $CsHSO_4$[31] **(C4)**, $[1,2\text{-dihydro-}1,3\text{-dimethyl-}2\text{-oxo-pyrimidinium}][HSO_4]$[32] **(C5)**, and **B10** in which screw and glide aggregates coexist. Only one compound, **C1**, was observed to crystallize in a polar space group. The aggregate type was determined even though coordinates of the hydrogen atom of the anion were not available. S-O contacts (1.592, 1.451, 1.448, 1.426 Å) were used to place the single hydrogen atom of the anion. All six screw aggregates are manifested as crystallographic 2_1 screw axes.

TABLE II Summary of the Type B (Glide Aggregate) Salts

Cation Code[a]	Compound Type[b]	Space Group	Polar	Interionic Distances (Å)	Source[c]
B1 2,4,6-collidinium	org	$Pna2_1$	Y	S-S: 4.52760(15) O-O: 2.599(4) N-O: 2.768(5)	This study
B2 2,4-lutidinium	org	$Pca2_1$	Y	S-S: 4.4437(10), 4.4382(9) O-O: 2.593(11), 2.622(10) N-O: 2.726(13), 2.728(12)	This study
B3 4,4'-bipyridinium	org	$P2_1/c$	N	S-S: 4.5121(23) O-O: 2.561(8) N-O: 2.814(9)	This study
B4 2-aminobenzimidazoloium	org	$P2_1/c$	N	S-S: 4.5180(18) O-O: 2.616(5) N-O: 2.814(9)	This study
B5 5,7-diphenyl-1,3-diazatricyclo [3.3.1.1]decan-6-one	org	$Pca2_1$	Y	S-S: 4.071 O-O: 2.536 N-O: 2.798	JADVIT
B6 phenanthrolinium	org	$P112_1/b$	N	S-S: 4.414 O-O: 2.564 N-O: 2.717	PHOLHS01
B7 hydroxytriphenylarsonium	orgm	$P2_1/c$	N	S-S: 4.551 O-O: 2.671 O-O[d]: 2.507	TADXIF
B8 benzotriazolium	org	Pbcn	N	S-S: 4.542 O-O: 2.645 N-O: 2.687, 2.705	BZTAZL
B9 hydronium	inorg	$P2_1/c$	N	S-S: 4.264 O-O: 2.658	Ref. 27
B10[e] 2-amino-5-nitropyridinium	org	Pcab	N	S-S: 4.660 O-O: 2.574 N-O: 2.771, 2.976	WANTUA
B11[f] K^+	inorg	Pbca	N	S-S: 4.533 O-O: 2.607	Ref. 12c
B12 $[K_{0.55}Rb_{0.45}]^+$	inorg	$P2_1/c$	N	S-S: 4.417 O-O: 2.547	Ref. 28

a: Cation identity based upon name in CSD if appropriate, b: org = organic cation, orgm = organometallic cation, inorg = inorganic cation c: 6-letter codes are those of the Cambridge Structural Database; d: O-O contact is between cation and anion; e: Glide and screw aggregates coexist in this structure; f: Glide and dimer aggregates coexist in this structure.

Inversion Aggregates: The 19 compounds which crystallize as inversion or type **D** aggregates are summarized in Table IV: [4-dimethylaminopyridinium][HSO$_4$] **(D1)**, [2,6-dimethoxypyridinium][HSO$_4$] **(D2)**, [(3,4,3',4'-bis(ethylenedithio-2,2',5,5'-tetrathiafulvalenium)][HSO$_4$]·0.5(3,4,3'4'-bis(ethylenedithio-2,2'5,5'-tetrathiafulvalene))[33] **(D3)**, [5,6-dihydro-1,4-dithiine-2,3-dithiolato-nickel(III)][HSO$_4$]·0.5(5,6-dihydro-1,4-dithiine-2,3-dithiolato-nickel(II))[34] **(D4)**, [triphenylmethylphosphonium][HSO$_4$][35] **(D5)**, [rel(1R, 2R, 4S, 5S)-2,5-dimethyl-1-(2-phenylethyl)-4-(N-propionylanilino)piperidium][HSO$_4$][36] **(D6)**, [3-carboxy-2-naphthalene-diazonium][HSO$_4$]·H$_2$O[37] **(D7)**, [berberine][HSO$_4$][38] **(D8)**, [3,7-dimethyl-1,5-diphenyl-3-aza-7-azoniabicyclo(3.3.1)nonan-9-one][HSO$_4$]·0.5H$_2$O[39] **(D9)**, [1,3,3-trimethyl-2,3-dihydro-1,2,4-triazolo(5,4-a)-4'-chlorophthalazine][HSO$_4$][40] **(D10)**, [tris(p-tolyl)-selenium][HSO$_4$][41] **(D11)**, [9-phenylacridi-

TABLE III Summary of Type C (Screw Aggregate) Salts

Cation Code[a]	Compound Type[b]	Space Group	Polar	Interionic Distances (Å)	Source[c]
C1 3,5-diphenyl-1,2-dithiolium	org	$P2_12_12_1$	Y	S-S: 4.497 O-O: 2.613	KUXSEB
C2 4-hydroxypyridinium	org	$P2_1/n$	N	S-S: 4.6659(10) O-O: 2.6052(24) O-O[d]: 2.6078(24) N-O: 2.919(3)	This study
C3 4,6-dimethyoxy-7-methyl-5H-furo (3,2-g)(1)benzopyran-5-one	org	$P2_1/c$	N	S-S: 4.466 O-O: 2.679 O-O[d]: 2.506	SEJLIC
C4 Cs^+	inorg	$P2_1/c$	N	S-S: 4.733 O-O: 2.554	Ref 31
C5 1,2-dihydro-1,3-dimethyl-2-oxo-pyrimidinium	org	$P2_1/n$	N	S-S: 4.931 O-O: 2.551	CIHVIY
B10[e]	org	Pcab	N	S-S: 4.690, O-O: 2.577, N-O: 2.878	WANTUA

a: Cation identity based upon name in CSD if appropriate; b: org = organic cation, inorg = inorganic cation c: 6-letter codes are those of the Cambridge Structural Database; d: O-O contact is between cation and anion; e: Screw and glide aggregates coexist in this structure.

nium(red)]$[HSO_4]$[42] **(D12)**, [9-phenylacridinium(green)]$[HSO_4]$[42] **(D13)**, α-$NaHSO_4$[43] **(D14)**, β-$NaHSO_4$[44] **(D15)**, [4b,5,15b,16-tetrahydrodibenzo(3,4,7,8)(1,5)diazocino(2,1-b:6,5-b)diquinazoline-11,22-di-ium]$[HSO_4]_2$[45] **(D16)**, and [3-phenoxypyridinium]$[HSO_4]$[46] **(D17)**. **B11** and **B12** are cocrystals of dimer and glide aggregates. The dimer motif is undesirable in the context of bulk polarity since it is predisposed towards centrosymmetry. Indeed, in all but one compound, the centre of gravity of the dimer coincides with a crystallographic centre of inversion, thereby precluding bulk polarity. Eleven of 16 salts have cations that may be considered bulky whereas the remainder have sterically undemanding cations.[47] Interestingly, of the 27 salts which exist as strands only, 6 may be considered to have bulky cations and 21 non-bulky cations.[48] This data clearly suggests that the presence of a bulky cation predisposes the salt towards dimer rather than strand formation. Such an assertion can be rationalized when one considers that the upper limit of S....S distances in strand aggregates is 4.931 Å (**C5**). In other words, cations which cannot efficiently stack within *ca.* 4.9 Å for type **A** aggregates or *ca.* 9.9 Å for type **B** or **C** aggregates should mitigate against strand formation.

Other Aggregates: Figure 4 illustrates three motifs which do not correspond to simple crystallographic operations: an inversion generated strand aggregate (**D17**, Figure 4a); a dimer with an attachment (**D14**, Figure 4b); a slipped dimer (**D15**, Figure 4c). **D17** crystallizes as a strand, but adjacent anions are generated *via* crystallographic inversion centres. The hydrogen atom involved in the O-H....O hydrogen bond is either disordered or located equidistant between two anions. A similar situation occurs in **B11**. Given the tendency for disorder of protons to generate centrosymmetry under ambient conditions[49], it is a salient observation that we encountered only two examples of disordered protons in compounds that crystallize as strand motifs. Three of the compounds that crystallize as dimers appear to have disordered hydrogen atoms: **D11, D14, D16**. Disorder is of little consequence in dimer

TABLE IV Summary of the Type D (Inversion Aggregate) Salts

Cation Code[a]	Compound Type[b]	Space Group	Polar	Interionic Distances	Source[c]
D1 4-dimethylamino pyridinium	org	$P2_1/n$	N	S-S: 4.043(3) O-O: 2.622(5) N-O: 2.841(5)	This study
D2 2,6-dimethoxy pyridinium	org	$P2_1/c$	N	S-S: 4.102(3) O-O: 2.583(5) N-O: 2.696(5)	This study
D3 3,4,3',4'-bis(ethylenedithio-2,2'-5,5'-tetra thiafulvalenium	org	P-1	N	S-S: 4.175 O-O: 2.605	FOYKUZ
D4 5,6-dihydro-1,4-dithiine-2,3-dithiolato-Ni(II)	inorg	P-1	N	S-S: 4.241 O-O: 2.615	YAWJAH
D5 triphenylmethyl phosphonium	org	$P2_1/c$	N	S-S: 3.966 O-O: 2.584	VAJXUZ
D6 [rel(1R,2R,4S,5S)-2,5-dimethyl-1-(2-phenylethyl) -4-(N-propionylanilino)piperidinium	org	P-1	N	S-S: 4.526 O-O: 2.655 N-O: 2.730	JINPAX
D7 3-carboxy-2-napthalene-diazonium	org	P-1	N	S-S: 4.544 O-O: 3.185 O-O[d]: 2.613	CNAPZS
D8 berberine	org	F-1	N	S-S: 4.301 O-O: 2.513	CISREB
D9 3,7-dimethyl-1,5-diphenyl-3-aza-7-azoniabicyclo (3.3.1)nonan-9-one	org	$P2_1/c$	N	S-S: 4.108 O-O: 2.614	BUHBIP
D10 1,3,3-trimethyl-2,3-dihydro-1,2,4-triazolo(5,4-a)-4'-chlorophthalazine	org	$P2_1/c$	N	S-S: 4.174 O-O: 2.598 N-O: 2.953	BOYHOM
D11 tris(p-tolyl)Se	orgm	$P112_1/b$	N	S-S: 4.129 O-O: 2.581	BORWAG
D12 9-phenyl acridinium (red)	org	$P2_1/c$	N	S-S: 4.169 O-O: 5.592 N-O: 2.753	Ref. 42
D13 9-phenyl acridinium(green)	org	P-1	N	S-S: 4.16 O-O: 2.64 N-O: 2.69	Ref. 42
D14[e] Na^+	inorg	P-1	N	S-S: 4.364 O-O: 2.692	Ref. 43
D15[f] Na^+	inorg	$P2_1/n$	N	S-S: 3.819 O-O: 2.671	Ref. 44
D16[g] 4b,5,15b,16-tetrahydrodibenzo(3,4,7,8)(1,5)diazocino (2,1-b:6,5-b)diquinazoline-11,22-di-ium	org	Pmmn	N	S-S: 4.261 O-O: 2.479, 2.513	GATMUJ
D17[h] 3-phenoxy pyridinium	org	$P2_1/c$	N	S-S: 4.921, 4.814 O-O: 2.574, 2.582 N-O: 2.722	GETGUH
B11[i]	inorg	Pbca	N	S-S: 4.290 O-O: 2.607	Ref 12c
B12[i]	inorg	$P2_1/c$	N	S-S: 4.409 O-O: 2.615	Ref 28

a: Cation identity based upon name in CSD if appropriate; b: org = organic cation, inorg = inorganic cation, orgm = organometallic cation; c: 6-letter codes are those of the Cambridge Structural Database; d: O-O contact is between cation and anion e: This structure exhibits a dimer *with an attachment (see text for details)*; f: This dimer is slipped; g: This dimer is not generated by an inversion center; h: This structure exists as a strand aggregate, its units related by inversion centres; i: Dimer and glide aggregates co-exist in this structure.

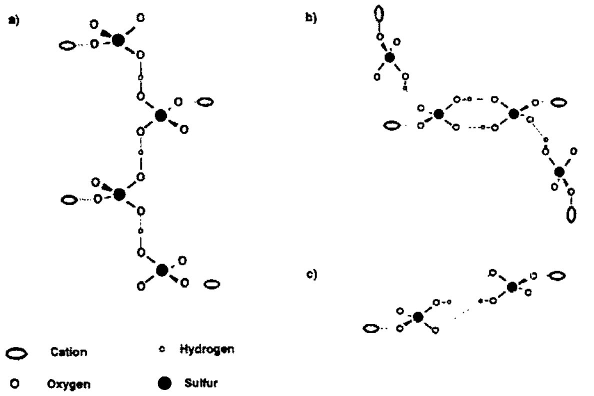

FIGURE 4 Schematic representation of the three alternate aggregates encountered in this study: inversion related strand aggregate **(a)**, dimer with an attachment **(b)** and slipped dimer **(c)**.

aggregates since a centre of inversion tends to occur even if there is no disorder. **D15** has a particularly short S....S contact because of the packing allowed by the alternative dimer motif. The value of 3.382 Å is much less than the average of the other dimers: 4.233 Å. A fourth anomaly is **D16**, a disordered structure in which the anions form a dimer aggregate and the solid as a whole is nonpolar. However, the two components of the dimer are crystallographically distinct and there are therefore two independent O....O contacts (2.479 and 2.513 Å).

New Hydrogensulfate Salts

The 10 new hydrogensulfate salts reported herein are based upon pyridinium cations and provide examples of all 4 classes of aggregate. The anions self-assemble *via* O-H....O hydrogen bonds, with O....O contacts ranging from 2.487(7) to 2.660(5) Å. Such contact distances define[50] the interactions as "very strong" to "strong" O-H....O hydrogen bonds. The N-H....O hydrogen bonds between cations and anions exhibit N....O contacts ranging from 2.696(5) to 2.934(5) Å. C-H....O hydrogen bonds were defined as those C....O contacts less than 3.40 Å exhibiting a C-H-O angle of between 90 and 180 degrees.[51] Only the closest contacts fitting these criteria were considered to be structure influencing.

Translation Aggregates: The hydrogensulfate anions of **A3** (Figure 5) and **A4** (Figure 6) self-assemble *via* hydrogen bonds (O .... O: 2.487(7) and 2.505(5) Å, respectively) to afford polar strands that align parallel to the a-axis. The intrastrand distances between sulfur atoms, 4.588(3) and 4.637(2) Å for **A3** and **A4**, respectively, therefore correspond to the lengths of the a-axis. The cations are N-H....O hydrogen bonded to the anions (N....O: 2.862(12) and 2.859(7) Å, for **A3** and **A4**, respectively) and are related by translation (Figures 7 and 8). The interplanar distances (3.53 and 3.76 Å, respectively) are indicative of π-stacking.[52] Each cation is involved in two types of C-H....O hydrogen bond: chelate (C....O: 3.102(20) Å for **A3**; 3.093(9) Å for **A4**) and cross-linking interactions. **A3** exhibits a short C-H....O hydrogen bond between adjacent strands (C....O: 3.193(20) Å) whereas **A4** exhibits two such interactions (C....O: 3.318(9) and 3.308(8) Å). Adjacent anionic strands are anti-parallel, however, the nitrogen atoms of the cations align roughly parallel to one another. Crystals of **A3** and **A4** therefore possess bulk polarity (space group $P2_1$, Figures 9 and 10).

A2 (Figure 11) exhibits several anomalous characteristics that were not observed in any of the other salts described herein. Two crystallographically independent anions self-assemble *via* strong hydrogen bonds (O....O: 2.660(5) and 2.566(5) Å), resulting in polar strands that run diagonally across the a-b plane (intrastrand

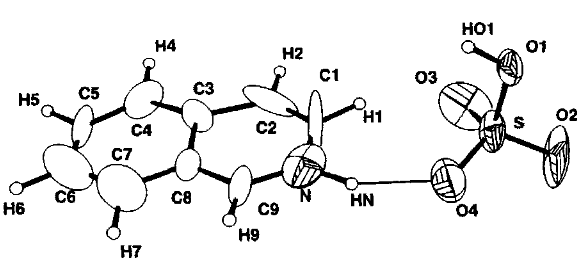

FIGURE 5 Labelled ORTEP of **A3**.

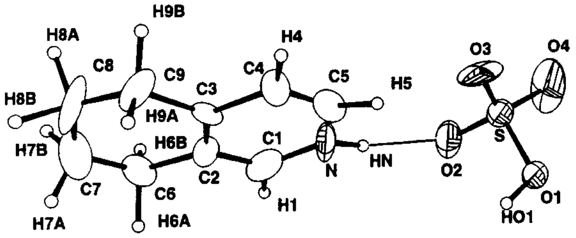

FIGURE 6 Labelled ORTEP of **A4**.

S....S: 4.795(3) and 4.834(3) Å, Figure 12). The cation hydrogen bonds to the anion *via* a bifurcated hydrogen bond, the only clear example of such encountered in this study. Adjacent anionic strands are bridged by cations, each of which form two N-H....O hydrogen bonds of comparable length with anions from different strands (N....O: 2.845(5) and 2.934(5) Å; 2.893(5) and 2.906(5) Å), thereby cross-linking the strands to yield sheets parallel to the a-b plane Figure 13). Anionic strands within sheets align parallel to one another, however, those in adjacent sheets are anti-parallel. **A2** therefore forms polar sheets but there is no bulk polarity and crystallization occurs in the centrosymmetric space group P-1. Seven close C....O contacts which fit the criteria for C-H....O hydrogen bonds are observed. Another anomaly is the observation that the plane of the cations is approximately parallel to the axis of the anionic strand (Figure 13). The strand

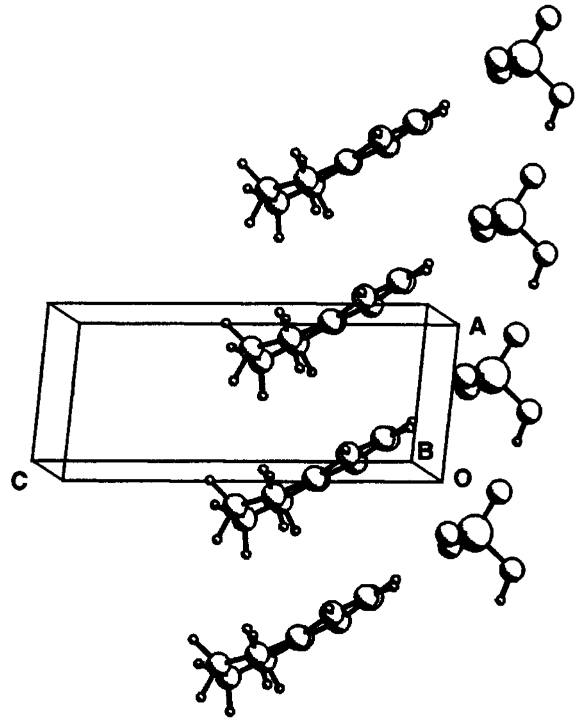

FIGURE 8 PLUTO plot of a single strand of **A4**.

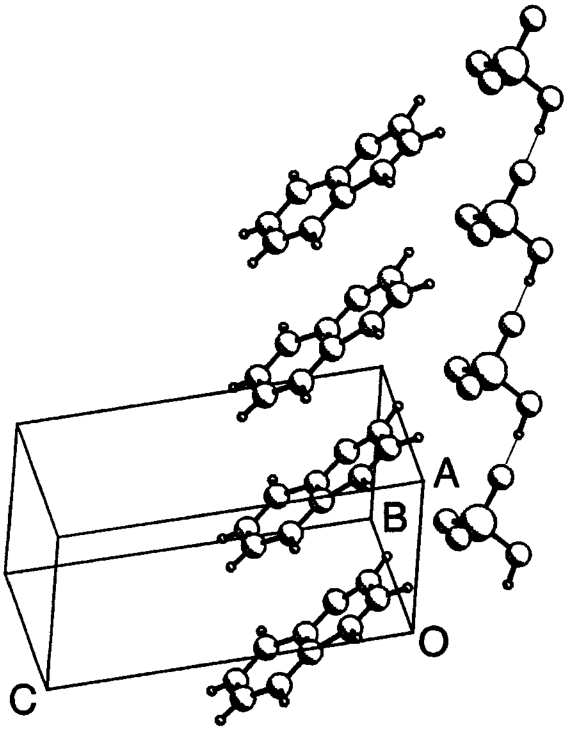

FIGURE 7 PLUTO plot of a single strand of **A3**.

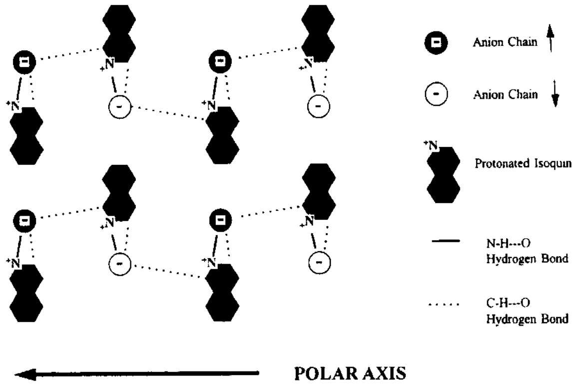

FIGURE 9 Schematic view of the 2-D sheet of **A3** that is generated by cross-linking of adjacent strands by C-H....O hydrogen bonds. Polarity is a result of the alignment of cations.

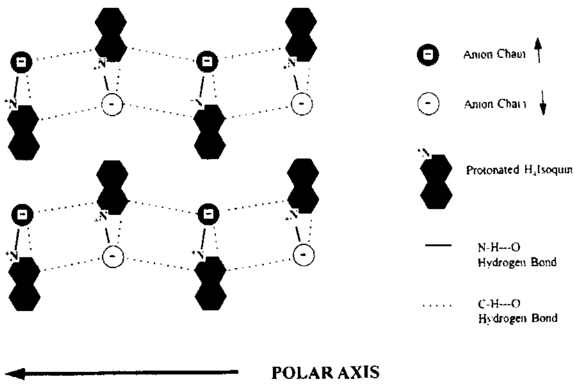

FIGURE 10 Schematic view of the 2-D sheet of **A4** that is generated by cross-linking of adjacent strands by C-H....O hydrogen bonds. Polarity is due to the alignment of the cations.

may be classified as a translation aggregate if one considers the repeating unit to be composed of $[\text{cation}]_2[HSO_4]_2$.

Glide Aggregates: Four of the new salts may be classified as type B aggregates: **B1** (Figure 14), **B2** (Figure 15), **B3** (Figure 16), and **B4** (Figure 17). The anions self-assemble (O....O: 2.599(4), 2.561(8) and 2.616(6) Å, respectively, for **B1**, **B3**, and **B4**; **B2** is discussed in a subsequent paragraph) into polar strands. These strands align with the c, c, and a-axes, respectively, and intrastrand S....S distances are 4.5276(15), 4.5121(23) and 4.5180(18) Å, respectively. Cations are hydrogen bonded to the anions *via* the protonated nitrogen atom (N....O: 2.768(5), 2.814(9) and 2.831(6) Å, respectively). The other N - H moiety of the cationic portion of **B3** is hydrogen bonded to an adjacent strand (N....O: 2.814(9) Å). **B4** also exhibits hydrogen bonding between the other two N-H hydrogen atoms of each cation and anionic strands, effectively cross-linking adjacent strands (N....O: 2.875(5) and 2.799(5) Å). This cross-linking generates an inversion centre between adjacent strands and results in loss of bulk polarity (Figures 18 and 19).

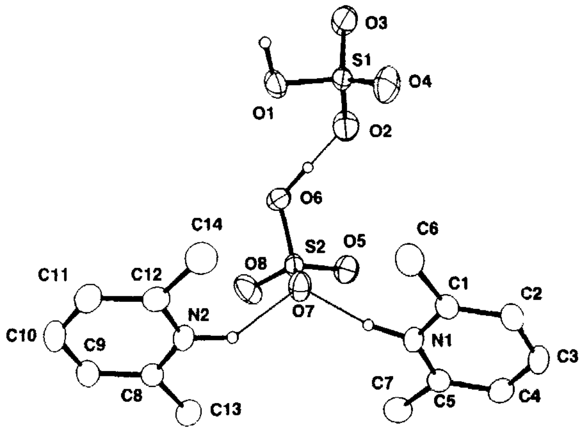

FIGURE 11 Labelled ORTEP of **A2**.

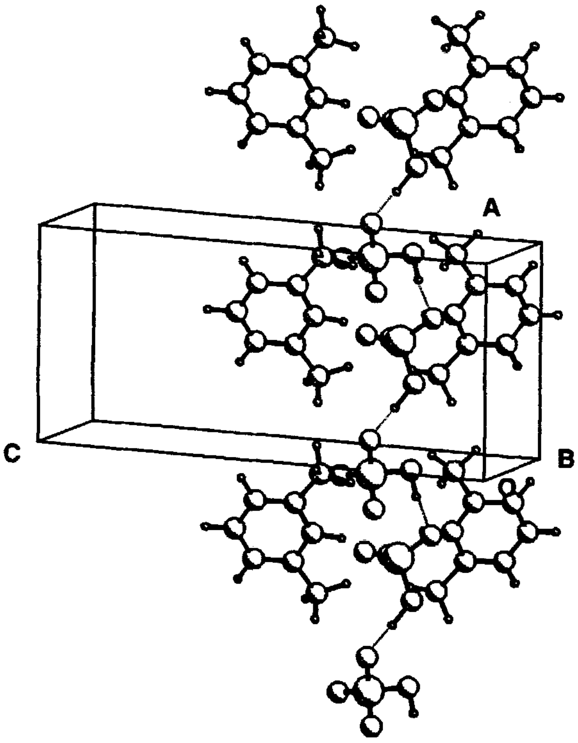

FIGURE 12 PLUTO plot of a single strand of **A2**.

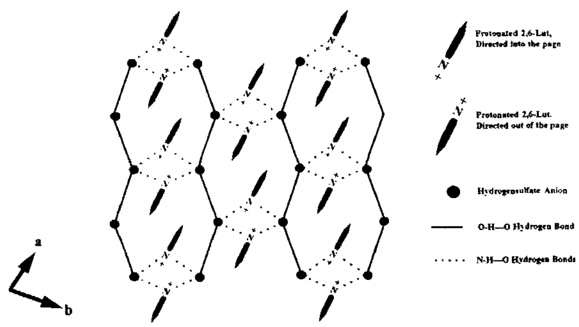

FIGURE 13 ORTEP view of the 2-D sheet of **A2** generated by cross-linking of adjacent strands by bifurcated N-H....O hydrogen bonds.

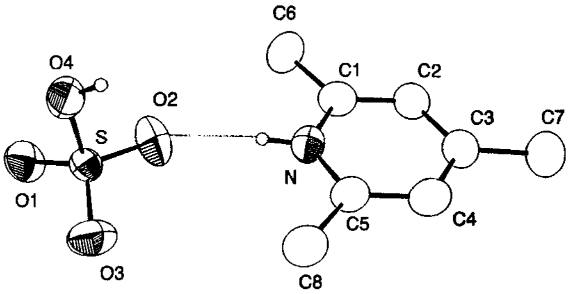

FIGURE 14 Labelled ORTEP of **B1**.

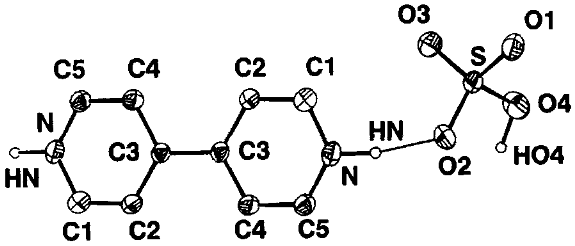

FIGURE 16 Labelled ORTEP of **B3**.

The cation of **B1** is incapable of forming more than one N-H....O hydrogen bond but does generate C-H....O hydrogen bonds that chelate (C....O: 3.249 Å) or cross-link (C....O: 3.334 Å) adjacent anionic strands. The cations stack with interplanar distances that are indicative of π-stacking, 3.58 Å.[52] Alternate cations flip *ca.* 180° with respect to the preceding cation, so that the C8 methyl group alternates. This is an important feature since the cross-linking *via* C-H....O hydrogen bonding manifests itself as a 3-D structure (Figure 20). Therefore, even though adjacent anionic strands are anti-parallel, the nitrogen atoms of the cations align throughout the structure, providing the directionality necessary for crystallization in a polar space group ($Pna2_1$).

The asymmetric unit of **B2** consists of two independent anions and cations which self-assemble into separate strands along the a-axis *via* hydrogen bonds (O....O: 2.593(11) and 2.622(10) Å, intrastrand S....S: 4.4437(10) and 4.4382(9) Å). The cations are hydrogen bonded to the anions (N....O: 2.726(13) and 2.728(12) Å) and alternate so that the 2-methyl group alternates along the a-axis (Figure 21). The crystallographically independent cations are both C-H....O hydrogen bonded to anions in adjacent strands. (C12....O1: 3.167(13); C4....O8: 3.325(13); C5....O8: 3.311(12) Å). The alternating orientation of the cations, which is similar to that observed in **B1**, once again generates 3-D architecture, a polar axis (Figure 21) and crystallization in the space group $Pna2_1$.

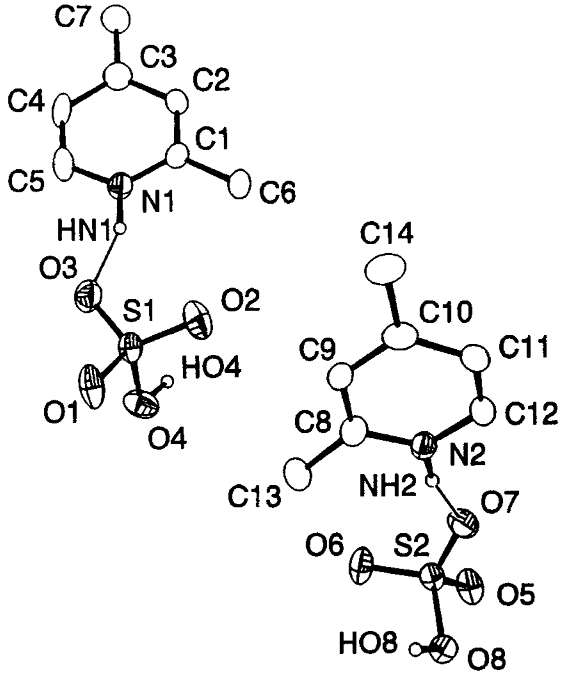

FIGURE 15 Labelled ORTEP of **B2**.

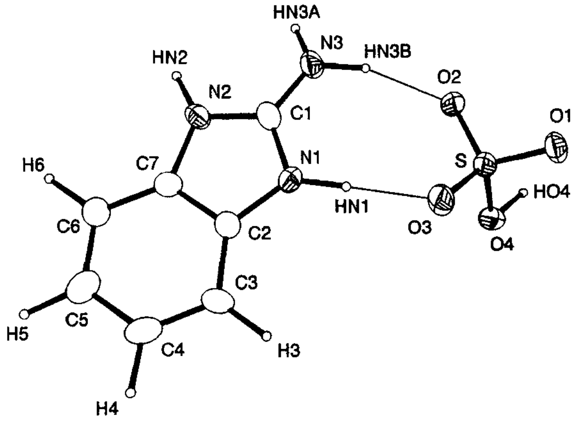

FIGURE 17 Labelled ORTEP of **B4**.

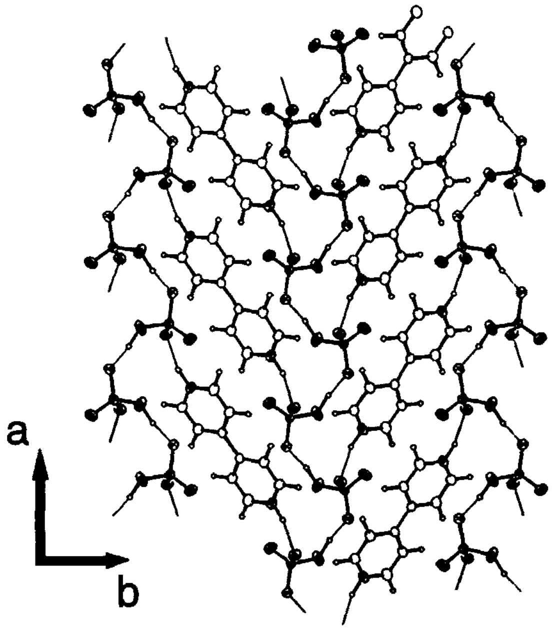

FIGURE 18 ORTEP view of the 2-D sheet of **B3** generated by cross-linking of adjacent strands by N-H....O hydrogen bonds.

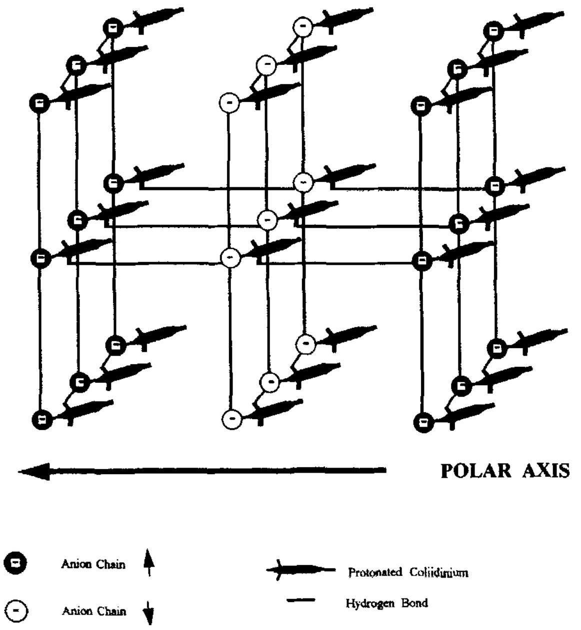

FIGURE 20 Schematic representation of the 3-D architecture of **B1**. C-H....O hydrogen bonds from the C8 methyl group cross-link the strands to generate a 3-D motif.

Screw Aggregates: Only one of the 10 newly synthesized salts, **C2** (Figure 22), generates a 2_1 screw aggregate. The anions self-assemble *via* O-H....O hydrogen bonds (O....O: 2.6052(24) Å, intrastrand S....S: 4.6659(10) Å) to yield polar strands. The cations form O-H....O and N-H....O hydrogen bonds with the anions, the protonated nitrogen and the 4-hydroxy group providing hydrogen bond donors (O....O: 2.6078(24) Å, N....O: 2.919(3) Å). This results in cross-linking of adjacent strands (Figure 23) similar to that observed in **B3**, cancellation of individual polarity, and crystallization in a centrosymmetric space group ($P2_1/n$).

Inversion Aggregates: **D1** and **D2** exist as dimer aggregates (Figures 24 and 25). The sulfur atoms are closer to one another than in the poly-

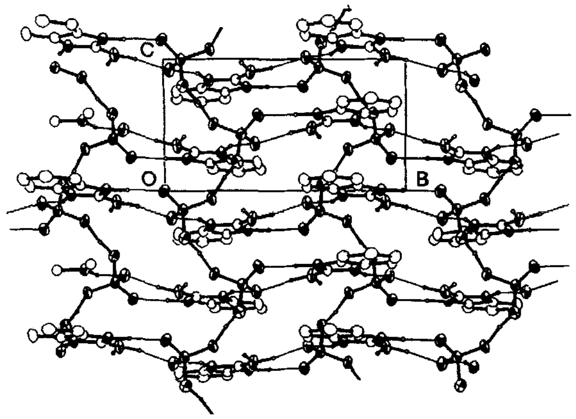

FIGURE 19 ORTEP view of the 2-D sheet of **B4** generated by cross-linking of adjacent strands by N-H....O hydrogen bonds.

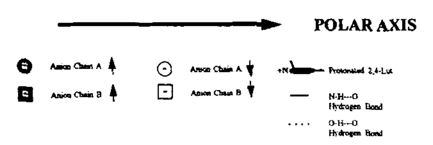

FIGURE 21 Schematic representation of the alternating orientation of cations in **B2** which, because of the roughly parallel alignment of nitrogen atoms, results in a polar axis.

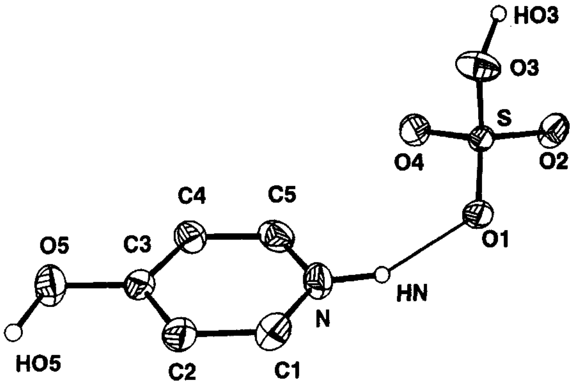

FIGURE 22 Labelled ORTEP of **C2**.

meric strands (S....S: 4.043(3) and 4.101(3) Å, for **D1** and **D2**, respectively), but O-H....O hydrogen bonds between dimer components are comparable to those of the strands (O....O: 2.622(5) and 2.583(5) Å, respectively). The cations are N-H....O hydrogen bonded to the anions (N....O: 2.841(5) and 2.696(5) Å, respectively) and dimers are linked into sheets by C-H....O hydrogen bonds (Figures 26 and 27, C....O: 3.207(6) and 3.281(6) Å, respectively). The centre of symmetry of the dimer coincides with a crystallographic centre of inversion. Therefore, neither the aggregate nor the bulk solid are polar (space groups are $P2_1/n$ and $P2_1/c$).

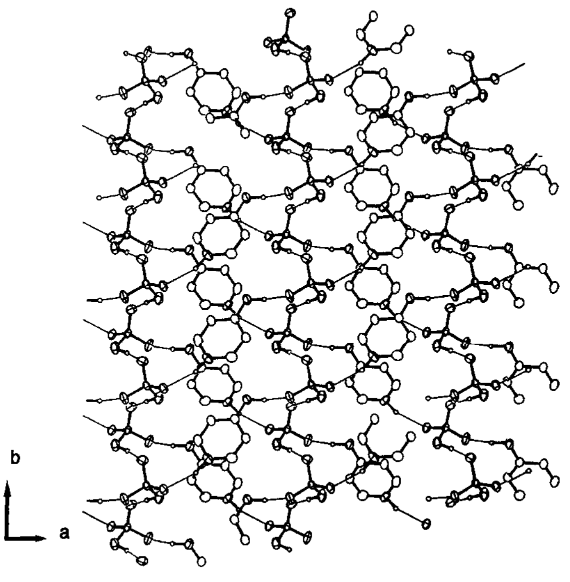

FIGURE 23 ORTEP view of the 2-D sheet of **C2** generated by cross-linking of adjacent strands by O-H....O hydrogen bonds.

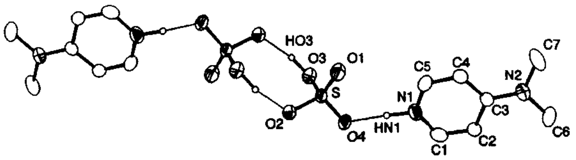

FIGURE 24 Labelled ORTEP of **D1**.

CONCLUSIONS

In conclusion, it is clear that the hydrogensulfate anion is indeed a suitable simple, inexpensive building block for the construction of polar solids since polar strand motifs are generated in the majority of crystal structures of hydrogensulfate salts. Furthermore, disorder of the proton of the hydrogensulfate anion is not prevalent in structures that adopt the strand motif. However, it is not clear from this study how to control either of the following: which of the three likely strand motifs is adopted; whether adjacent strands pack anti-parallel or parallel. Nevertheless, three observations could influence future work: the dimer motif, which is undesirable from the perspective of bulk polarity, tends to occur with bulky cations; the only structure that contains a chiral cation is also the only structure that exhibits the most desirable motif, the translation aggregate with parallel alignment of anions; in the

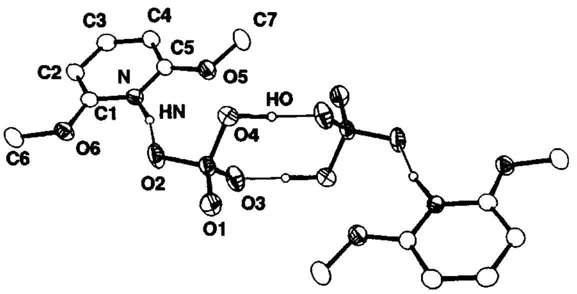

FIGURE 25 Labelled ORTEP of **D2**.

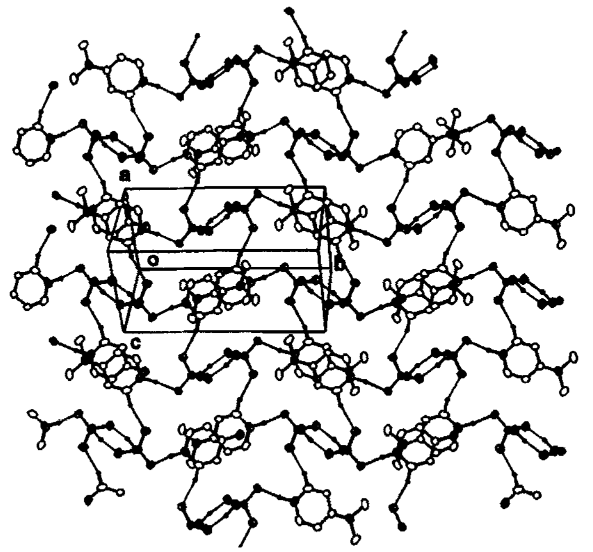

FIGURE 26 ORTEP view of the 2-D sheet of **D1** that is generated by the linking of individual dimers by C-H....O hydrogen bonds.

absence of strong hydrogen bond donors, packing of adjacent strands is controlled by C-H....O hydrogen bonds.

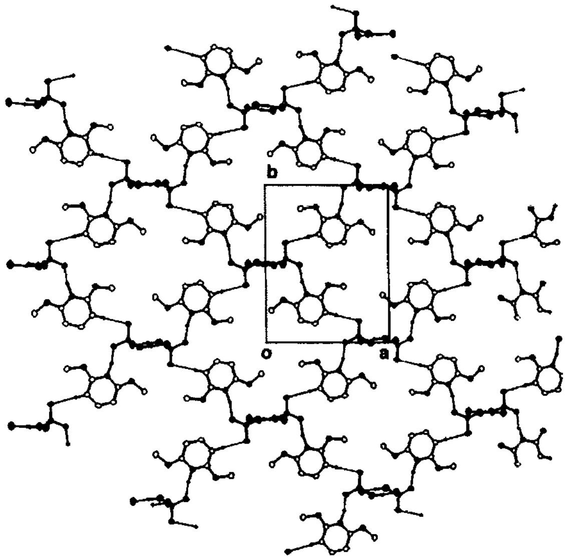

FIGURE 27 ORTEP view of the 2-D sheet of **D2** that is generated by the linking of individual dimers by C-H....O hydrogen bonds.

EXPERIMENTAL SECTION

All reagents and solvents were purchased from the Aldrich Chemical Company. Reagents were used without further purification with the exception of 2,4-lutidine. Solvents were dried and distilled before use. Hydrogensulfate salts, with the exception of **B2** and **B3**, were prepared by dissolving the appropriate base in methanol, adding approximately one equivalent of H_2SO_4 (17.8 M) dropwise from a syringe, and stirring the solution at room temperature. Solvent was removed via rotoevaporation. Crude samples of **A2, A4, B2, C2** and **D2** were observed to be hygroscopic.

A2: 4.0 mL (34.3 mmol) of 2,6-lutidine and 2.1 mL (37.4 mmol) of H_2SO_4 were dissolved in 50 mL of methanol and stirred for 4 hours. A yellow wet solid was afforded which, upon storage in a desiccator, formed a dry solid. Single crystals of **A2** were obtained from a methanol solution layered with hexanes at −15°C. mp: 158–160°C. IR (cm^{-1}): 3301 (O-H....O); 2907 (Ar-H); 2350 ($N\text{-}H^+$); 1624 (C=N); 1552, 1465, 1410 (C-C); 1159, 1027 (broad, HSO_4^-); 850, 790, 713.

A3: As for **A2** but 3.0 mL (25.5 mmol) of isoquinoline and 1.6 mL (28.5 mmol) of H_2SO_4 were dissolved in 50 mL of methanol and stirred for approximately 12 hours. A light brown solid was generated from which single crystals were obtained from a methanol solution layered with hexanes at room temperature. mp: 207–209°C. IR (cm^{-1}): 3390 (strong and broad O-H....O); 3071 (Ar-H); 2668, 2349 ($N\text{-}H^+$); 1651 (C=N); 1616-1392 (C-C); 1375 (S=O); 1233, 1033 (broad, HSO_4^-); 839, 800, 770, 751.

A4: As for **A2** but 3.0 mL (23.2 mmol) of 5,6,7,8-tetrahydroisoquinoline and 1.5 mL (26.7 mmol) of H_2SO_4 were dissolved in 50 mL of methanol and stirred for approximately 4 hours. An orange wet solid was afforded which, upon storage in a desiccator, formed a dry solid. Single crystals were obtained from an acetonitrile solution layered with hexanes and cooled to −15°C. mp: 153–155°C. IR (cm^{-1}): 3370 (broad, O-H....O); 2940 (strong C-H); 2613 (broad N-H$^+$); 1632 (C=N); 1532, 1487 (C=C); 1107 (HSO_4^-); 1034, 980, 926, 896, 829, 761, 734, 700, 684, 670.

B1: As for **A2** but 5.0 mL of 2,4,6-collidine (3.8 mmol) and 2.3 mL (4.1 mmol) of H_2SO_4 were dissolved in 50 mL of methanol and stirred for approximately 4 hours. A peach coloured dry solid was afforded. Single crystals were obtained from methanol at room temperature. mp: 198–200°C. IR (cm^{-1}): 3302 (N-H....O); 3067 (strong and broad, O-H....O, C-H); 2348 (N-H$^+$); 1655, 1632 (C=N); 1506, 1525 (C=C); 1228, 1163, 1102 (HSO_4^-), 1043, 932, 853.

B2: 2,4-lutidine was distilled prior to use. 2.0 mL (17 mmol) of 2,4-lutidine and 0.97 mL of H_2SO_4 (17 mmol) were combined without solvent. The reaction was exothermic, and upon cooling a pink solid formed. Single crystals were grown from acetonitrile. mp: 79–81°C. IR (cm^{-1}): very broad and centered at approximately 3000 (C-H, O-H....O, N-H....O); 2344 (N-H$^+$); 1640 (C=N); 1542, 1490 (C-C); 1234, 1055 (HSO_4^-); 878, 824, 768, 686.

B3: Crystals of **B3** were obtained from a co-crystallization attempt in 50 mL of methanol of the products of the following 2 reactions: 1.01 g (6.4 mmol) of 4,4'-dipyridyl and 0.36 mL (6.4 mmol) of H_2SO_4 in 25 mL of methanol; and 2.00 g (12.8 mmol) of 4,4'-dipyridyl and 1.10 mL of HCl (12.7 mmol), in 25 mL of methanol. mp: does not melt below 300°C. IR (cm^{-1}): 3049, (broad O-H....O, C-H); 2118 (N-H$^+$); 1630, 1595 (C=N, C=C); 1500, 1484, 1458 (C-C); 1225, 1193, 1024 (HSO_4^-); 958, 843, 798, 762.

B4: As for **A2**, but 1.0 g (7.5 mmol) of 2-aminobenzimidazole and 0.42 mL (7.5 mmol) of H_2SO_4 were dissolved in 25 mL of methanol and stirred for approximately 15 minutes at room temperature. Rotoevaporation yielded a light pink powder. Single crystals were grown from a methanol solution layered over chloroform at 5°C. mp: 189–192°C. IR (cm^{-1}): very broad and centered at approximately 3000 (C-H, O-H....O, N-H....O); 2482 (N-H$^+$); 1689, 1605 (C=N); 1527, 1474, 1412 (C-C); 1305 (S=O); 1271, 1206, 1150, 1049 (HSO_4^-); 1024, 888, 741.

C2: As for **A2**, but 2.0 g (21 mmol) of 4-hydroxypyridine and 1.2 mL (21 mmol) of H_2SO_4 were dissolved in 25 mL of methanol. Rotoevaporation yielded a thick yellow liquid which solidified upon standing for approximately 6 hours. Single crystals of **C2** were obtained from acetonitrile at room temperature. mp: 92–93°C. IR (cm^{-1}): broad and centered at 2863 (C-H, and O-H....O); 1636, 1608 (C=N, and C=C); 1547, 1508 (C-N, and C-C); 1321 (S=O); 1220, 1192, 1054, (HSO_4^-); 1006, 882, 849, 816.

D1: As for **A2** but 1.0 g (8.2 mmol) of 4-dimethylaminopyridine and 0.45 mL (8.0 mmol) of H_2SO_4 were dissolved in methanol and stirred for approximately 15 minutes. A thick brown oil containing yellow crystals formed and was washed with toluene. Single crystals of **D1** were obtained from an acetonitrile solution of the yellow crystals layered with hexanes at −15°C. mp: 199–201°C. IR (cm^{-1}): 3226 (N-H....O); 3071 ($-CH_3$); 2943 (Ar-H); 2326 (N-H$^+$); 1688, 1643, 1598 (C=N, and C=C); 1565, 1445, 1404 (C-N, and C-C); 1306 (S=O); 1208, 1169, 1063 (HSO_4^-); 992, 942, 882, 851, 815.

D2: As for **A2** but 4.0 mL (27.3 mmol) of 2,6-dimethoxypyridine and 1.9 mL (33.8 mmol) of H_2SO_4 were dissolved in 50 mL of methanol and stirred for 4 hours. A pink solid was obtained from which single crystals of **D2** were grown from a tetrahydrofuran solution layered with hexanes at −15°C. mp: 130–132°C. IR (cm^{-1}): 3101-2621 (strong and very broad, C-H, O-H, Ar-H); 2346, 2300 (N-H$^+$); 1657 (C=N); 1640 (C=C); 1380 (C-C); 1349 (S=O); 1278, 1176 (HSO_4^-); 1082, 1012, 974, 867, 802, 787, 729, 660.

TABLE V Crystallographic Data for A2, A3, A4, B1, B2, B3, B4, C2, D1 and D2

salt	A2	A3	A4	B1	B2	B3	B4	C2	D1	D2
formula	$SO_4NC_7H_{11}$	$SO_4NC_9H_9$	$SO_4NC_9H_{11}$	$SO_4NC_8H_{13}$	$SO_4NC_7H_{11}$	$S_2O_8N_2C_{10}H_{12}$	$SO_4N_3C_7H_9$	$SO_5NC_5H_7$	$SO_4N_2C_7H_{12}$	$SO_6NC_{77}H_{11}$
formula weight	205.2	227.2	231.3	219.2	205.2	352.3	231.2	193.2	220.2	237.2
a, Å	8.2420(24	4.588(15	4.6372(22)	9.055(3)	8.8525(17)	5.8297(6)	10.8556(10)	9.1587(9)	8.1422(16)	11.114(4)
b, Å	8.182(3)	10.067(4)	10.0353(13)	9.832(3)	10.0891(18)	16.8197(13)	13.0479(9)	5.5518(4)	14.825(3)	13.9658(18)
c, Å	16.200(4)	10.720(4)	11.281(3)	11.495(3)	21.097(3)	7.2602(10)	7.0776(9)	14.9982(22)	8.2965(15)	6.703(4)
α, deg	85.18(5)	90	90	90	90	90	90	90	90	90
β, deg	79.00(6)	100.58(6)	95.51(4)	90	90	103.561(15)	98.908(20)	100.531(24)	101.04(3)	104.36
γ, deg	60.27(2)	90	90	90	90	90	90	90	90	90
V, Å^3	931.2(4)	486.7(3)	522.6(3)	1023.4(5)	1884.3(6)	692.04(13)	990.04(13)	749.77(14)	983.0(3)	1007.9(7)
Z	4	2	2	4	8	2	4	4	4	4
cryst. dim, mm	0.80×0.50×0.30	0.20×0.30×0.70	0.10×0.40×0.60	0.20×0.20×0.50	0.10×0.30×0.40	0.10×0.50×0.60	0.15×0.30×0.40	0.20×0.40×0.50	0.40×0.40×0.40	0.15×0.30×0.60
space group	P -1	P 2_1	P 2_1	P na2_1	P ca2_1	P 2_1/c	P 2_1/c	P 2_1/n	P 2_1/n	P 2_1/c
radiation	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a	MoKα^a
μ, cm^{-1}	3.2	3.1	2.9	2.9	3.1	4.1	3.1	4.0	3.1	3.2
trams. range		0.750-0.999	0.667-0.994		0.686-0.963	0.67-1.00	0.706-0.998	0.845-0.935		0.717-0.9236
scan mode	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
2θ max, deg	44.8	45.0	49.8	50.0	49.8	49.9	44.9	49.8	44.9	44.9
# reflns collected	2426	848	1833	947	1700	1218	1287	1230	1274	1306
# reflns observed	2198^b	638^c	1407^c	742^c	1251^c	936^b	864^b	1072^c	971^c	1065^c
# variables	235	136	136	134	235	108	136	109	130	136
R_f	0.054	0.066	0.068	0.028	0.065	0.063	0.050	0.031	0.048	0.047
R_w	0.065	0.056	0.060	0.032	0.067	0.079	0.046	0.042	0.049	0.046
G.O.F.	8.77	5.87	7.39	1.89	3.90	7.51	2.28	3.28	3.98	5.52

a: (λ = 0.70930Å), b: $I > 2.5\sigma(I)$, c: $I > 3.0\sigma(I)$.

X-ray Crystallography

Single crystals suitable for X-ray crystallography were mounted and sealed in glass capillaries and optically centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer (**A2**, **A3**, **A4**, **B2**, **B3**, **B4**, **C2**, **D1** and **D2**), or a Siemens P3 diffractometer (**B1**). The structures were solved using direct methods. All non - hydrogen atoms were located *via* difference Fourier map inspection as were the methyl, N-H and O-H hydrogen atoms of **A2**, **A3**, **A4**, **B1**, **B4**, **C2**, **D1** and **D2**. All planar hydrogen atoms bonded to aromatic carbons were calculated, $D_{C\text{-}H}$ = 1.00 (**A2**, **A3**, **A4**, **B1**, **B2**, **C2** and **D2**) and 1.08 Å (**B3**, **B4** and **D1**). Hydrogen atoms were not refined with the exception of the N-H and O-H hydrogen atoms of **B1** and **B3** (also located *via* difference Fourier map inspection), and the O-H hydrogen atom of **D1**. O-H and N-H hydrogen atoms of **B2** were calculated with $D_{C\text{-}H}$ = 1.08 Å. All hydrogen atoms were assigned isotropic thermal parameters based upon the atom to which they are bonded. Friedel equivalents were collected and included in least squares refinement for **A4** only and the enantiomorph was fixed by refining chirality eta[53] to 1.531. The enantiomorph of **A3** was fixed by refining chirality eta to 1.585. Details of crystal data, data collection, and structure refinement are presented in Table V. Weights based upon counting statistics were used with the weight modifier, k in kF_0^2, being determined *via* evaluation of variation in the standard reflections that were obtained during the course of data collection. Values of R and R_w were given by $R = \Sigma\ (|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma(w|F_o| - |F_c|)^2/\Sigma(wF_o)^2]^{1/2}$. Tables of final fractional coordinates, interatomic bond distances and angles have been submitted as supplementary material. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[54] locally implemented on an IBM compatible 80486 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).[55] Crystallographic figures were generated using ORTEP[56] and PLUTO[54]. Atomic coordinates and anisotropic thermal parameters are available from the Cambridge Structural Database.

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