Uronium sulfonate module as a topological director for a polar layer arrangement

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Uronium and sulfonate ions are demonstrated to self-assemble into two-dimensional hydrogen-bonded polar sheets. The ancillary benzene rings attached to the sulfonate ions are aligned on one side of the sheets. The whole directional and topological information for recognition and two-dimensional organisation is implicated for the supramolecular unit with general formula $[(NH_2)_2COH]^+[RSO_3]^-$. Although the uronium and the sulfonate moieties are mismatched in terms of symmetry and numbers of hydrogen bonding atoms, the aggregation of ionic and non-polar regions leads to the formation of a lamellar structure. The van der Waals interactions intercalating the hydrogen-bonded sheets into lamellae dictate cancellation of the net dipole moment in the intralamellar space.

Crystal engineering means finding an algorithm for a predictable and controllable long-range molecular organisation resulting in a well defined crystal network with potentially useful physical and chemical properties.[1] Basically, the crystal structure of a material is a result of iterative self-assembling of the constituent molecular, co-molecular[2] or ion pair subunits, considered as fundamental crystal building units. However, the prediction of the solid-state structure of crystals is commonly frustrated by the complexity and lack of directionality of intermolecular forces.[3] Consequently, crystal engineering at the present time is focused mainly on establishing the relationships between molecular and supramolecular levels *via* intermolecular interactions.[4] The chemical aspect of the design problem appraises the choice and formation of chemical units that acquire structure determining information, which is crucial for a strategic network generation. Formation of extended networks requires polyvalent functionalities of the units, which, in effect, makes the packing control in three-dimensions elusive owing to the numerous possible intermolecular interactions and multiplicity of structural possibilities. Therefore, the structural aspect accounts for the interplay between such factors as directional demands of the interactions and geometrical dictates of the close-packing, which more often are in conflict than in consonance for the required balance in ordered solid-state networks with desired arrangement and dimensionality. A reasonable strategy for surmounting these obstacles is to use supramolecular synthons[5] or modules,[6] capable of formation of robust hydrogen-bonded multi-dimensional networks. Intelligent choice of *n*-dimensional modules serving as 'topological directors' allows the crystal engineering problem to be reduced to $3-n$ dimensions.

Recently organic salts have been broadly used in the design of layered and/or porous solids. A series of ammonium salts of trimesic and trimelitic acids $[R_2NH_2][HTMA]$ and $[R_2NH_2]_2[HTML]$ have been reported by Zaworotko and coworkers[7] to form robust hydrogen-bonded two-dimensional supramolecular sheets. The dialkylammonium salts generate interdigitated lamellar structures, whereas salts with R = benzyl facilitate incorporation of solvent or aromatic guests in between the sheets. Ward and coworkers[6,8] used the guanidinium sulfonate $[Gn^+RSO_3^-]$ module to design hydrogen-bonded sheets, intercalatively layered in an R-dependent manner or covalently bonded in sterically controlled clathrate host frameworks. Analogous hydrogen-bonded sheets gener-

ated by the isostructural $[Gn^+NO_3^-]$ unit are observed in the guanidinum nitrate crystal structure.[9] Apparently, the ion pairs $[Gn^+XO_3^-]$ are capable of maintaining their dimensionality and general structural features not only upon changes in ancillary functional groups, but also in the presence of other molecular species in the lattice. Therefore, they can be used as universal two-dimensional modules for crystal engineering. A generalisation can be made that the inherent modular nature of the synthon is predominantly dependent upon the topological similarity of the constituents. Another important factor is how much different will the synthon become (and the generated two-dimensional network) if its geometry is modified by lowering the symmetry of one of the constituent ions. Replacement of one amino group in the guanidinium ion (Gn^+) **I** with a hydroxy group leads to the formation of the uronium ion (Ur^+) **II** (Chart 1). The different symmetry and the mixed bonding functionality of **II** should modify the hydrogen-bond connectivity patterns. The hydrogen-bonded ring motif, described by the graph set $R_2^2(8)$,[10] formed by the two amino groups of urea will be maintained whereas the motif formed by the hydroxy group should change. Consequently, the topology and the recognition features of the whole ion pair should be quite different. Analysis of the ion pair size and shape, as well as the hydrogen-bond formation capabilities and preferences outlined the polar chain arrangement as a first step of organisation. The high symmetry of **I** allows the mirror related hydrogen atoms to access the lone pairs located on two oxygens of the next sulfonate group in order to form the identical hydrogen-bonded ring motif $R_2^2(8)$.[6] Only a single hydrogen-bond donor site is available in **II** for one-dimensional propagation which should effect chain formation as in **IV** *cf.* the ribbon extension **III**. The topology of the hydrogen-bond donors and acceptors, not used in the chain (ribbon) formation, accommodates the parallel alignment of these chains (ribbons). However, owing to the different symmetry constraints in **II** and **I**, the resultant two-dimensional modules **VI** and **V** executing the crystal networks should be substantially different. Whereas the guanidinium sulfonate module is pseudo-hexagonal, the uronium sulfonate module should be non-centrosymmetric.

These types of speculation, aimed at an elaboration of a reliable strategy for a controllable polar alignment of urea subunits in three-dimensional solid-state structures, are understandable when considering the important non-linear optical
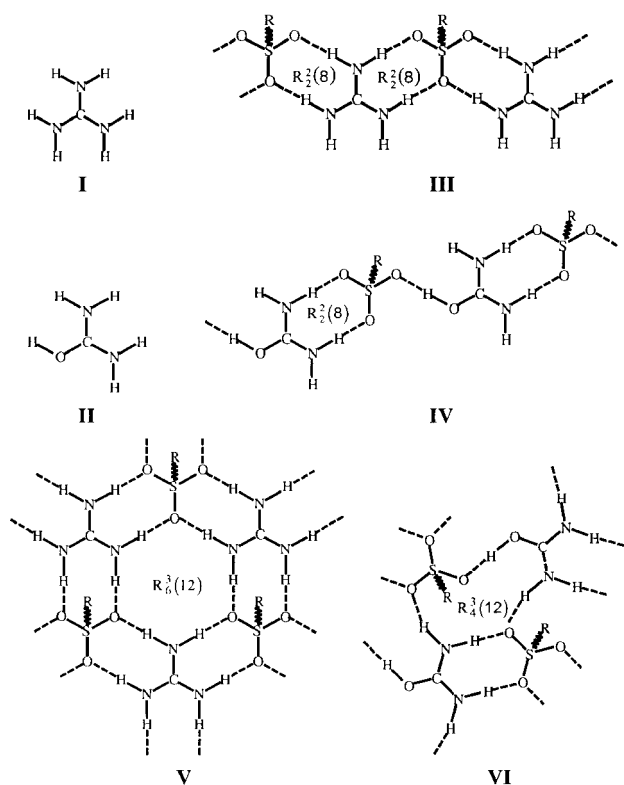
Chart 1

mulls and compared with those of the starting materials. Single-crystal X-ray structural data for **1** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) using the ω-scan technique at 24 °C. Lattice parameters were obtained from least-squares analysis of 25 reflections ($21.2 < 2\theta < 33.6°$). The intensity of three standard reflections, measured every 75 min remained constant through the data collections, indicating crystal and electronic stability. The structure was corrected for Lorentz, polarisation and secondary extinction effects and solved by direct methods with MITHRIL[14] and DIRDIF[15] with refinement by least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement parameters while all hydrogen atoms were refined isotropically. The hydrogen atom attached to the urea oxygen was included at the difference map, but was not refined.
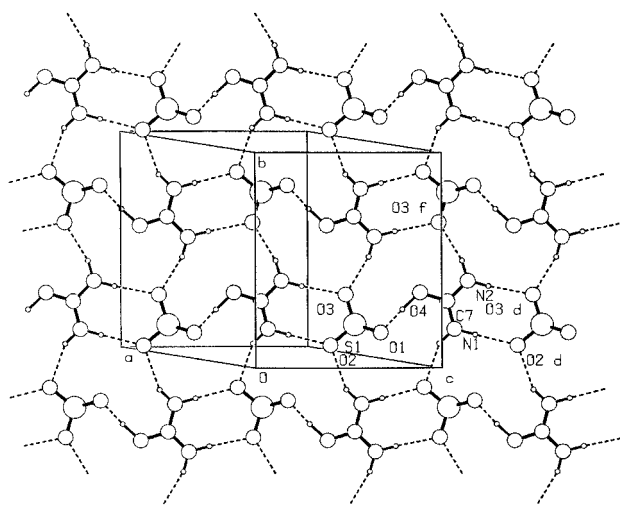
Crystal data. $C_7H_{10}SO_4N_2$, $M_r = 218.23$, colourless plate ($0.60 \times 0.50 \times 0.10$ mm), monoclinic, space group $C2/c$ (no. 15), $a = 24.430(9)$, $b = 9.810(3)$, $c = 8.390(4)$ Å, $\beta = 109.85(4)°$, $V = 1891(3)$ Å^3, $Z = 8$, $D_c = 1.533$ Mg m^{-3}, $T = 297$ K, $F(000) = 912$, $\mu = 0.318$ mm^{-1}; 3319 measured reflections ($2\theta_{max} = 50.0°$), 1662 independent reflections ($R_{int} = 0.051$); refinement on F for 1405 reflections [$I > \sigma(I)$], and 128 parameters, $R = 0.073$, $wR = 0.104$.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/193.

Results and discussion

Vibrational analysis

The measured melting points of 155 °C for **1** and 150 °C for **2** are higher than those for the parent compounds (135 ° for urea, 65–66 °C for benzenesulfonic acid and 92–95 °C for *p*-toluenesulfonic acid). This fact suggests that the proton is transferred from the sulfonic to the urea moiety, with a resultant hydrogen-bond bridged salt formation instead of a hydrogen-bonded cocrystal. The proton transfer was consequently confirmed by the IR spectra which are identical for both studied compounds **1** and **2**. The most spectacular changes, observed in the region of the very strong hydrogen bond ν(OH) stretching vibration, as well as in the region of the NH$_2$ stretching and deformation modes, confirm the formation of the postulated comolecular unit. The broad absorption (3500–1500 cm^{-1}) exhibiting an A, B, C structure, characteristic for the spectra of sulfonic acids exhibiting a very strong hydrogen-bond system with a proton tunnelling through the barrier of a double well potential undergoes a significant narrowing in the cocrystal spectra.[16] The broad, single band centred at 2246 cm^{-1} reflects the formation of a new noncentrosymmetric strong hydrogen bond (O–H$^+\cdots$O$^-$) connecting the constituents into the postulated ion pair. In addition, the deformation OH modes are shifted to 1468 cm^{-1} [δ(OH)] and 874 cm^{-1} [γ(OH)] in **1** and **2** (*cf.* 1494 and 906 cm^{-1} in the constituent sulfonic acids). The ν(C=O) mode wavenumber decrease of 119 cm^{-1} (1567 cm^{-1} in the cocrystal *cf.* 1686 cm^{-1} in pure urea) reflects the significant elongation of the carbonyl bond due to protonation of the urea moiety. The dramatic changes observed in the region of the NH$_2$ stretching and deformation modes, also evidence the formation of new hydrogen bonds completely different from those in urea. The red shift of the stretching modes from 3450 to 3374 cm^{-1} [ν_a(NH$_2$)] and from 3340, 3261 cm^{-1} to 3219, 3184 cm^{-1} [ν_s(NH$_2$)] establishes that the heteromolecular hydrogen-bond interactions between the urea amino groups and the sulfonic groups are stronger than the homomolecular

properties of urea.[11] A search in the Cambridge Structural Database[12] (CSD) has revealed that the crystal structure of uronium nitrate consists of hydrogen-bonded polar layers, stacked in the third dimension by van der Waals interactions.[13] Stimulated by the assumption of topological and directional similarity of the [Ur$^+$XO$_3{}^-$] units (X = N, S), we postulate that the replacement of the sulfonate ion for the nitrate ion should also lead to formation of a polar two-dimensional hydrogen-bonded network. If this premise is correct, the design problem of an acentric material may than be reduced to a one-dimensional problem, dependent upon an appropriate functionalisation of the sulfonate ancillae R, which do not disturb the polar orientation of urea. In order to establish the topological similarity of the [Ur$^+$RSO$_3{}^-$] unit and verify the polarity of the two-dimensional hydrogen-bonded network, we have synthesised and studied the simplest representatives of uronium sulfonate salts.

Experimental

Materials

All commercially available starting materials were purchased from Aldrich and used without further purification. Spectroscopic-grade solvents and/or deionised water were used for all crystallisations.

Synthesis

Uronium benzenesulfonate [(NH$_2$)$_2$COH]$^+$[C$_6$H$_5$SO$_3$]$^-$ **1**, and uronium toluene-*p*-sulfonate [(NH$_2$)$_2$COH]$^+$ [*p*-CH$_3$C$_6$H$_4$SO$_3$]$^-$ **2** crystals were grown from methanol solutions containing equimolar amounts of urea and benzenesulfonic (*p*-toluenesulfonic) acids using slow evaporation.

Characterisation

Melting points were determined with a Fisher–Johns apparatus (F–J) and are uncorrected. Solid state IR spectra were recorded on a Nicolet 510M spectrometer (4 cm^{-1} resolution) as Nujol

Fig. 1 The 2D organisation of the uronium and sulfonate ions leads to formation of the hydrogen-bonded network of the lamella surface. For clarity the aromatic rings in the third direction are omitted.

interactions of urea itself. This is not surprising, taking into consideration that the sulfonate oxygens are much better hydrogen bond acceptors[17] than the urea carbonyl oxygen. Subsequently, the deformation $\delta(NH_2)$ modes in the cocrystal experience a blue shift and appear at 1714 and 1672 cm^{-1} (*vs.* 1630 and 1602 cm^{-1} in pure urea). On the other hand, the carbonyl mode $\nu(C{=}O)$ undergoes decoupling from the $\delta(NH_2)$ modes and is observed as a single band located at significantly lower wavenumber. All these spectroscopic observations testify to an elongation of the urea carbonyl C=O bond with a simultaneous shortening of the amino N–H bonds during the cocrystallisation process. This is caused by new hydrogen-bond interactions that are distinctive from those in urea. On the other hand, the $\nu_1(SO_3)$ and $\nu_3(SO_3)$ stretching modes (1200–1000 cm^{-1})[18] split into five separate bands reflecting the dynamic behaviour of the sulfonate group participating in five different hydrogen bonds. These spectroscopic results are in excellent correlation with the crystallographic data (Table 1). Accordingly, the band at 1202 cm^{-1} is related to the vibration

of the longest S–O1 bond (1.459 Å) incorporated in the strongest hydrogen bond O4–H40···O1. The band pair 1152, 1130 cm^{-1} corresponds to the vibration of the S–O2 bond (1.448 Å) and the band pair at 1039, 1011 cm^{-1} corresponds to that of the S–O3 bond (1.434 Å). The band splitting, observed for the intermediate and the shortest S–O bonds, may be explained by correlation field effects, since each of the sulfonate oxygens O2 and O3 is sterically and topologically accessible to two different hydrogen bonds donated by the four urea amino-hydrogens (Table 2).

Crystal structure and hydrogen-bonded networks

The X-ray single crystal measurements reveal that the urea protons (*anti* positioned relative to the carbonyl bond C=O) exactly project towards the sulfonate oxygen lone pairs and thus promote the hydrogen-bonded dimer interaction **II** (Chart 1). The eight-membered hydrogen-bonded ring motif $R_2^2(8)$ formed *via* two amino nitrogen atoms of a single uronium ion and two lone pairs on two oxygen atoms of a single sulfonate ion (N1–H7···O2 and N2–H9···O3) is identical to that formed in guanidinium sulfonate **I**. However, the further aggregation of **I** and **II** is quite different owing to their different chemical and geometrical features. The deficiency of one hydrogen-bond donor on the uronium ion results in one-dimensional chain formation **IV** instead of ribbon formation **III**. Only one of the lone pairs located on the third oxygen of the sulfonate ion is sterically accessible for the hydroxy hydrogen of the translationally related uronium ion, in order to form a charge-assisted hydrogen bond O4–H40···O1. The peculiar recognition features of the uronium and guanidinium ions arising from their topology and symmetry differences are unveiled in the two-dimensional associations **VI** and **V**, which are considerably distinct from each other. The glide reflection operator appears to be the only interchain symmetry relation meeting the topological constraints and sterical demands, if the *syn* oriented urea protons are to interact with the lone pairs of the sulfonate oxygens in contiguous chains with a consequently polar alignment. The loose twelve-membered, ring motif $R_4^3(12)$ in **VI** encompasses both the intrachain (O4–H40···O1, N1–H7···O2 and N2–H9···O3) and interchain (N1–H8···O2 and N2–H10···O3) hydrogen bonds, and therefore, the whole

(a)

(b)
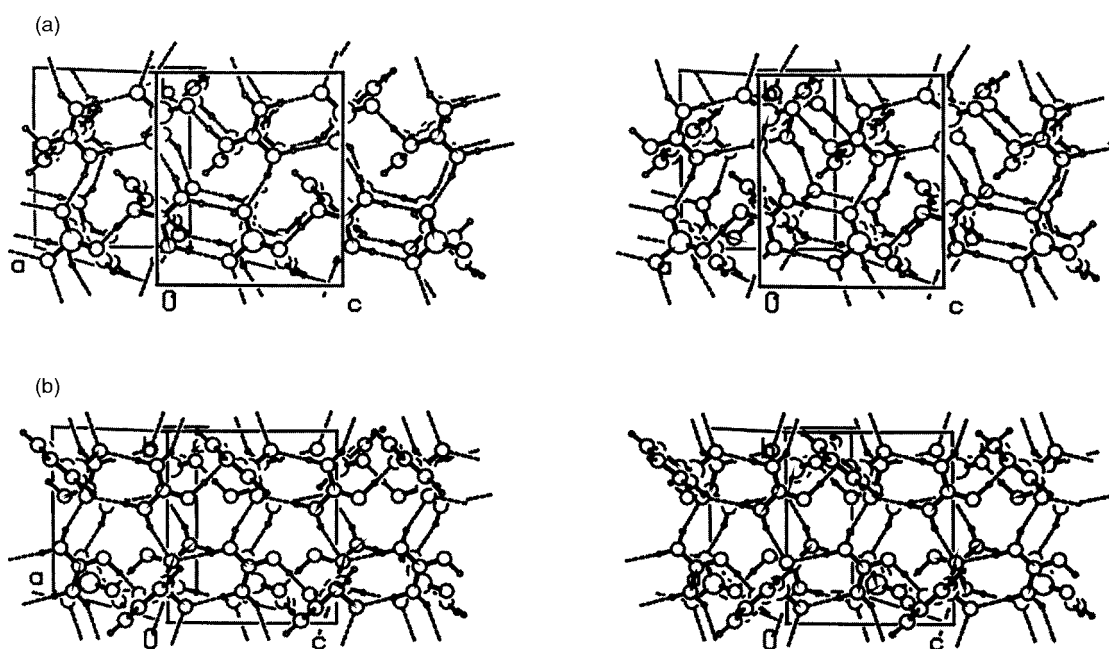
Fig. 2 Visualisation of the molecular assemblies forming the intralamellar (a) and interlamellar (b) regions in the uronium benzenesulfonate crystal.
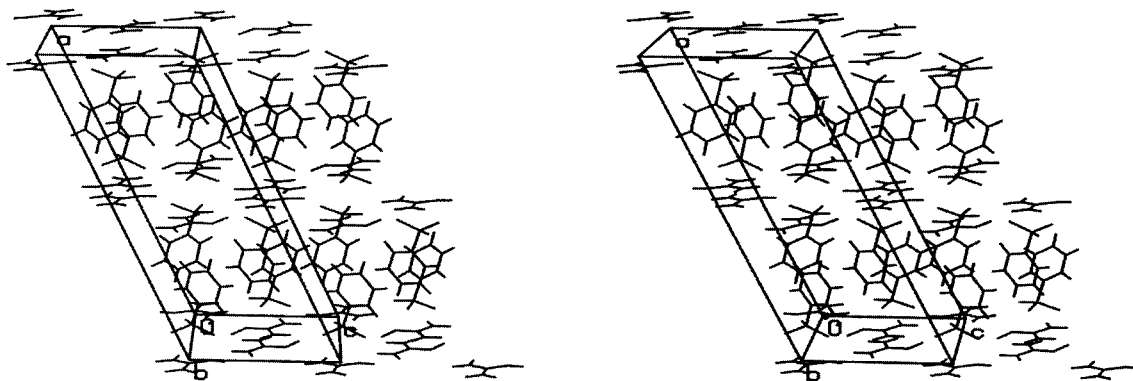
Fig. 3 A stereo picture of the three-dimensional crystal structure organisation.

Table 1 Selected bond distances (Å) and angles (°) in crystals of uronium benzenesulfonate **1** compared with those of urea

1		Urea[19]	
O4–H40	1.118		
C7–O4	1.278(7)	C=O	1.265(1)
C7–N1	1.307(7)	C–N1	1.350(1)
N1–H7	0.954	N1–H1(N1)	1.005(4)
N1–H8	0.947	N1–H2(N1)	0.997(5)
C7–N2	1.297(7)	C–N2	1.350(1)
N2–H9	0.949	N2–H1(N2)	1.005(4)
N2–H10	0.949	N2–H2(N2)	0.997(5)
S1–O1	1.459(4)		
S1–O2	1.448(4)		
S1–O3	1.434(4)		
S1–C1	1.778(6)		
C7–O4–H40	117.96	N1–C7–N2	121.3(5)
C7–N1–H7	119.75	O1–S1–O2	111.5(2)
C7–N1–H8	120.31	O1–S1–O3	113.0(2)
H7–N1–H8	119.94	O1–S1–C1	105.7(2)
C7–N2–H9	120.01	O2–S1–O3	112.8(2)
C7–N2–H10	119.80	O2–S1–C1	106.3(2)
H8–N2–H10	120.19	O3–S1–C1	106.9(2)
O4–C7–N1	121.9(5)	S1–C1–C2	119.5(4)
O4–C7–N2	116.8(5)	S1–C1–C6	119.0(4)

information for organisation in two dimensions [*cf.* the pseudo-hexagonal ring motif in $R_6^3(12)$ **V**]. The ancillary groups (R = benzene ring) are extended almost perpendicular to the hydrogen-bonded network and comply to the same symmetry rules that execute the chain and the monolayer arrangement. The glide reflection operator, governing the interactions between the chains, dictates edge-to-face configurations of the benzene rings with an average H···C distance of 3.234 Å. van der Waals interactions (average H···H distance of 2.962 Å) intercalate the sheets forcing interdigitation of the aromatic rings in the third dimension with a resultant densely packed bilayer (lamella) formation. On the other hand, coulombic interactions pack the lamellae into three-dimensional structural

formation. However, the symmetry inter-relations between the lamellae walls result in the net dipole moment cancellation in the observed crystal structure since the twofold screw rotation operator $2_1(y)$ is controlling both the intralamellar and the interlamellar regions. Fig. 1 shows the hydrogen-bonded polar sheet pervading the lamellae walls while Fig. 2 shows the intra- and inter-lamellar relations of the three-dimensional assembly and Fig. 3 shows the molecular organisation in the crystal structure. Selected bond lengths and angles of the crystal building module **1** compared with the bond parameters of urea[19] are summarised in Table 1. Full geometric information concerning the structure determining interactions in the cocrystal is presented in Table 2.

Conclusions

In the present study, we have demonstrated that replacement of the guanidinium ion with the uronium ion in sulfonate salts also leads to formation of hydrogen-bonded sheets. However, the mismatching of donor and acceptor sites placed on both counter ions leads to a significantly modified crystal organisation. The hydrogen-bonded sheets in the uronium sulfonate maintaining the polar orientation of urea can be perceived as a two-dimensional propagation of supramolecular units **VI** constituted by two ion pairs (Ur⁺RSO₃⁻). Whereas the module **V**, generating two-dimensional networks in guanidinium sulfonate salts, is quasi-hexagonal and consists of three symmetry matched ion pairs, module **VI** is inherently acentric because of the mismatched symmetry of the counter ions. The separation of the ionic and the non-polar van der Waals regions in the three-dimensional organisation (see Graphical Abstract) is an important feature driving the lamellar structure of the crystal. Similarly to guanidinum sulfonate salts, the extension in the third dimension depends upon the size, symmetry and functionality of the ancillary groups on the sulfonate ion. A controllable three-dimensional organisation with a useful crystal functionalisation may probably be accomplished by ingenious modifications of the non-polar

Table 2 Hydrogen bond geometry and aromatic interaction contact distances in crystals of uronium benzenesulfonate **1**

Intralayer interaction	D–H···A (Å)	D–H (Å)	H···A (Å)	Symmetry operator
O4–H40···O1	2.554(5)	1.118	1.493	*x*, *y*, *z*
N1–H7···O2	2.902(6)	0.954	1.949	*x*, *y*, −1+*z*
N2–H9···O3	2.959(6)	0.949	2.012	*x*, *y*, −1+*z*
N2–H10···O3	2.992(6)	0.949	2.083	*x*, 1−*y*, −1/2+*z*
N1–H8···O2	3.045(6)	0.947	2.184	*x*, −*y*, −1/2 +*z*
Interlayer interactions			Contact distance/Å	
C–H···π			H···C (av)	*x*, −*y*, −1/2+*z*
π···π			3.234	*x*, 1−*y*, −1/2+*z*
			H···H (av)	1/2−*x*, −1/2+*y*, 3/2−*z*
			2.962	

(intralamellar) region. Investigations along these guidelines are ongoing now.

Acknowledgements

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