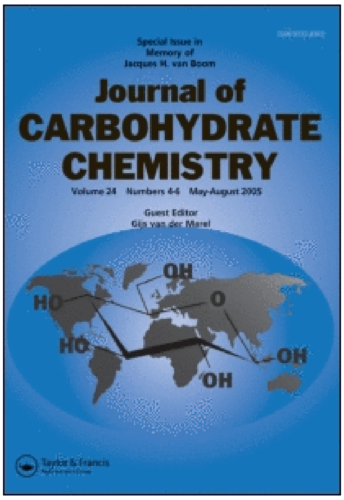

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Bevan P. Jarman[ab]; Donald E. Kiely[a]; M. Manley-Harris[b]; Brian K. Nicholson[b]
[a] Shafizadeh Rocky Mountain Center for Wood and Carbohydrate Chemistry, University of Montana, Missoula, Montana, USA [b] Chemistry Department, University of Waikato, Hamilton, New Zealand

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The Structures and Hydrogen Bonding Networks in Crystals of Alkylenediammonium Salts of Galactaric Acid

Bevan P. Jarman,[1] Donald E. Kiely,[2] M. Manley-Harris,[3] and Brian K. Nicholson[3]

[1]Shafizadeh Rocky Mountain Center for Wood and Carbohydrate Chemistry, University of Montana, Missoula, Montana, 59812, USA; and Chemistry Department, University of Waikato, Hamilton, New Zealand
[2]Shafizadeh Rocky Mountain Center for Wood and Carbohydrate Chemistry, University of Montana, Missoula, Montana, 59812, USA
[3]Chemistry Department, University of Waikato, Hamilton, New Zealand

The crystal structures of five alkylenediammonium galactarates (**1**–**5**) were determined because the information from these structures may provide some insight into the solid state structures of the poly(alkylene galactaramides) derived from these salts. In each case the *meso*-galactarate anion is in the extended conformation. In four out of the five cases associations between galactarate units led to alternating layers of anions and cations rather than the expected alternation of anion and cation found in ionic solids. All five salts display extensive hydrogen bonding involving ammonium and carboxylate groups and in some cases hydroxyl groups of the anion.

Keywords Crystal structures, Alkylenediammonium galactarates, Hydrogen bonding

INTRODUCTION

Alkylene and substituted alkylenediammonium galactarates are precursors of poly(alkylene galactaramides), a type of polyhydroxypolyamide (PHPA).[1,2]

PHPAs are of interest because they are derived, at least in part, from renewable carbohydrates, and they exhibit a range of different physical properties that include differences in polymer solubility, melting points, and physical appearance. These properties are intimately connected to the conformation of the contributory aldaric acid.[1] For example, the crystal structure of galactaric

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Address correspondence to M. Manley-Harris, Chemistry Department, University of Waikato, Hamilton, New Zealand. E-mail: manleyha@waikato.ac.nz

acid has been reported[3] and shows the molecule in an extended conformation and strongly hydrogen bonded. The acid has a high melting point (206°C)[3] and is insoluble in both water and organic solvents. Structures have also been reported for some inorganic salts of galactaric acid including lanthanides[4,5] and ammonium galactarate,[6] all of which show an extended conformation for the galactarate unit. Prior to this present work, there have been no structures reported for organic ammonium salts of galactaric acid and we now present five examples, **1–5** (Fig. 1). It is possible that the associations observed within the crystal structures of the salts may shed some light upon the three-dimensional association (or nonassociation) between monomer diacid units, diamine units, or diacid/diamine units in the poly(alkylene galactaramides) derived from these salts.

EXPERIMENTAL

Ethylene diammonium galactarate (**1**), tetramethylene diammonium galactarate (**2**), 3′,6′-dioxaoctamethylenediammonium galactarate (**3**),

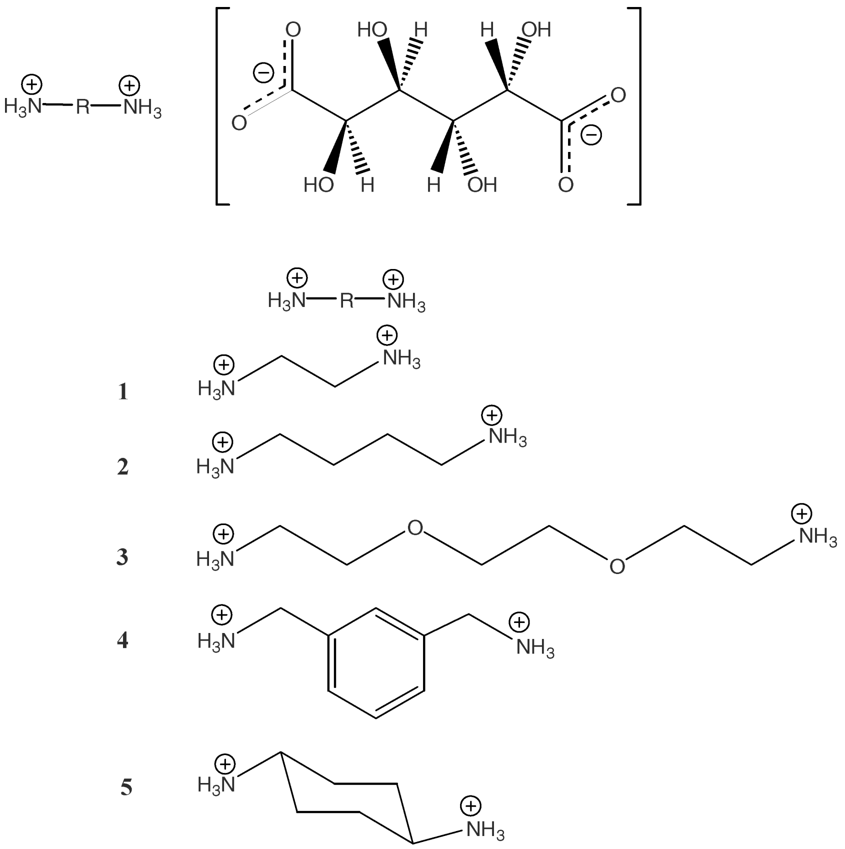

Figure 1: Structures of compounds **1–5**.

m-xylylenediammonium galactarate (**4**), and cyclohexyldiammonium galactarate (**5**) were prepared as described previously.[7]

Crystals of **1** and **4** suitable for x-ray analysis were obtained by refluxing the compounds in water, filtering while hot, and allowing the solution to cool slowly to rt.

Crystals of **2** and **3** suitable for x-ray analysis were obtained by slow evaporation of an aqueous solution, while those of **5** were obtained by vapor diffusion of ethanol into an aqueous solution.

X-ray Crystal Data

X-ray intensity data and crystal parameters were obtained on a Bruker SMART CCD diffractometer for **1–3**, and a Bruker Apex II CCD diffractometer for **4** and **5**. Data were corrected for absorption using SADABS,[8] and the structures were solved by direct methods (SHELXS-97) and refined on F_o^2 with all nonhydrogen atoms anisotropic (SHELXL-97),[9] operated under WinGX.[10] All hydrogen atoms were located from difference maps and were refined with isotropic temperature factors. Graphics were generated with ORTEP-III.[11]

Crystal data and refinement details are listed in Table 1.

RESULTS AND DISCUSSION

The crystal structure of galactaric acid has been reported[3] and shows a large network of strong hydrogen bonding with the carboxylic acid groups forming characteristic hydrogen-bonded dimers, and the hydroxyl groups bonding in a square fashion, which is noted for being particularly stable.[12,13] All of the hydroxyl groups are involved in cooperative H-bonding in that the OH groups all act as –O-H. . . O donors, and also –H. . . O-H acceptors, which enhances the strength of the bonding. These favorable hydrogen bonding motifs impart a remarkably high crystal density (1.79 g $\mathrm{cm^{-3}}$), a high melting point (206°C), and a low aqueous solubility to galactaric acid.[3]

The structures have been reported of some inorganic salts of galactaric acid, including derivatives of group 1 and 2 cations,[4] and of lanthanides.[5] For these, the crystal packing is dominated by chelating interactions of the oxygen atoms of the galactarate anion to the metal cations, with secondary hydrogen bonding interactions. For ammonium galactarate, the cation hydrogen bonds to four separate anions through two N-H. . . $O_{\mathrm{carboxylate}}$ and two N-H. . . O_{hydroxyl} hydrogen bonds, with each of the four C-O-H groups for each anion hydrogen bonded to $O_{\mathrm{carboxylate}}$ atoms of adjacent anions.[6] This network leads to a density of 1.62 g $\mathrm{cm^{-3}}$, significantly lower than for the acid itself, but the packing is still efficient with a volume of 15.6 Å^3/non-H atom (compared with the exceptionally low 13.8 in galactaric acid itself).

The five organic ammonium salts of galactaric acid described here are important as they may provide clues to the three-dimensional structures and

Table 1: Crystal data and refinement details for salts **1–5**.

	1.H_2O	**2**	**3.$2H_2O$**	**4.$2H_2O$**	**5**
Formula	$C_8H_{20}N_2O_9$	$C_{10}H_{22}N_2O_8$	$C_{12}H_{30}N_2O_{12}$	$C_{14}H_{26}N_2O_{10}$	$C_{12}H_{24}N_2O_8$
M_r	288.26	298.30	358.30	382.4	324.33
T(K)	89(2)	89(2)	89(2)	93(2)	93(2)
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a(Å)	10.286(1)	4.7491(4)	7.0140(1)	5.5384(2)	6.450(2)
b(Å)	9.929(1)	8.7068(8)	7.0393(1)	10.0965(4)	11.326(5)
c(Å)	12.996(1)	9.0173(8)	9.8913(2)	16.3307(6)	10.278(4)
α (deg)	90	61.498(1)	78.272(1)	104.300(1)	90
β (deg)	103.869(1)	89.857(1)	86.640(1)	92.779(1)	109.907(3)
γ (deg)	90	83.850(1)	73.762(1)	100.927(1)	90
V (Å^3)	1288.7(2)	325.28(5)	459.10(10)	864.48(6)	706.0(5)
Z	4	1	1	2	2
ρ (g cm^{-3})	1.486	1.523	1.426	1.469	1.526
μ (mm^{-1})	0.135	0.132	0.128	0.125	0.128
Size (mm^3)	0.32×0.28×0.26	0.26×0.20×0.12	0.36×0.28×0.22	0.55×0.30×0.14	0.22×0.17×0.10
F (000)	616	160	212	408	348
θ_{max}(deg)	26.4	26.4	26.3	27.5	27.3
Refln collected	11750	3106	4442	9640	3547
Tmax, min	0.976, 0.847	0.977, 0.616	0.954, 0.760	0.983, 0.934	0.987, 0.972
Unique reflns	2617(R_{int}0.019)	1320(R_{int} 0.025)	1863(R_{int} 0.014)	3890(R_{int} 0.018)	1428(R_{int} 0.064)
R_1 ($I > 2\sigma(I)$)	0.0342	0.0458	0.0302	0.0342	0.0349
wR_2 (all data)	0.0836	0.1105	0.0774	0.0865	0.0929
GOF on F^2	1.058	1.057	1.093	1.034	1.027
Final Δe (e Å^{-3})	0.37	0.30	0.36	0.46	0.23

hence physical properties of the PHPAs derived from them. All of the corresponding polyamides have been reported.[7]

Several features are common to all of the structures examined. Firstly, they are all present with the galactaric acid fully deprotonated to form a dicarboxylate anion and the fully protonated diammonium cation. The hydrogen atoms were located in the crystal structure determinations and these were unambiguously associated with the ammonium groups. Consistent with a delocalized carboxylate anion, the carbon-oxygen bond lengths were essentially equal. Furthermore, the C1–C2 carbon-carbon bonds (sp^2–sp^3 bond) vary between 1.5267(13) Å for C1–C2 in **3** and 1.5401(15) Å for C1–C2 in **1,** significantly longer than the equivalent of 1.513(2) Å in galactaric acid. This arises from the delocalization within the carboxylate group and has been reported to be a general phenomenon in a survey that showed that the average carbon-carbon bond length for C–COOH was 1.502(14), while for $C–COO^-$ it was 1.520(11).[14]

A second general feature is that the *meso*-galactarate ion is in the fully extended conformation for all of the salts **1–5**, which is expected as galactarate lacks unfavorable, 1,3-parallel eclipsing of hydroxyl groups, which, in other acyclic carbohydrates, can give rise to bent or "sickle" conformations;[15,16] the extended conformation was also found in earlier examples with inorganic cations. Figure 2 shows the anion found in **1** as a typical example for all five structures, showing the numbering scheme.

The C1-C2-C3-C4 and C3-C4-C5-C6 torsion angles are within ±7 degrees of 180 degrees and the α-hydroxy-carboxylate fragment always adopts the favored coplanar arrangement, to within ±0.06 Å, even when there is no intramolecular H^- bonding between the hydroxyl group on C2 and one of the carboxylate oxygen atoms. The hydroxyl groups on C2 and C3 (and equivalent C4, C5) adopt a *gauche* configuration (O2-C2-C3-O3 torsion angles 60 ± 10 degrees) and the hydroxyl groups on C3 and C4 are *anti* (O3-C3-C4-O4 torsion

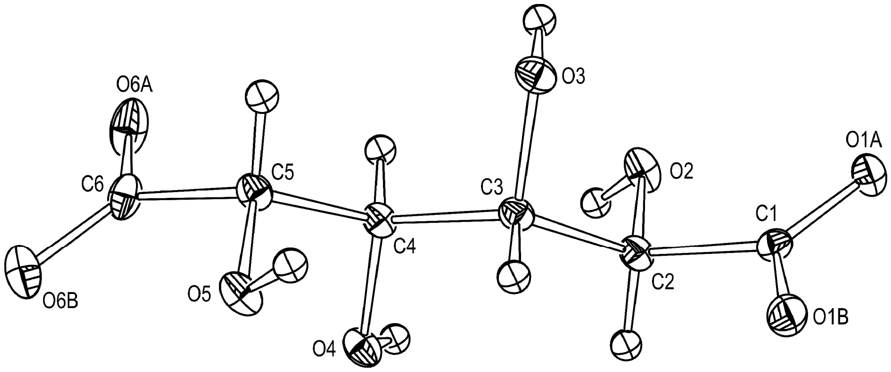

Figure 2: Structure and numbering scheme for the galactarate anion in **1**, which typifies the extended conformation found in **1–5**.

angles 180 ± 2 degrees). These general features are also found for the other salts reported,[4–6] and also for galactaric acid itself.[3] Clearly the crystal packing interactions with different cations are not sufficient to induce significant conformational changes from this strongly preferred orientation.

The main interest in the structures of **1–5** is in the H-bonding network adopted in each case. For these salts the –NH_3^+ groups will be donors, the $-COO^-$ group an acceptor, while the –O-H groups can act as both acceptor and donor. In addition, three of the five examples crystallize as hydrates, giving extra H-bonding interactions involving water molecules. Each structure will now be discussed in turn.

*H-bonding in 1,2-ethylenediammonium galactarate, **1***

The asymmetric unit of this salt consists of one cation, one anion, and a water molecule of crystallization, all in general positions; the crystal packing is shown in Figure 3. The H-bonding interactions are complicated, as shown in Figure 4, and lead to an entangled array of cations and anions.

For the cation, all three N-H bonds at each end of the ethylenediammonium act as donors, giving two strong H-bonds to carboxylate O atoms and a longer one to a C-O-H of adjacent anions in each case.

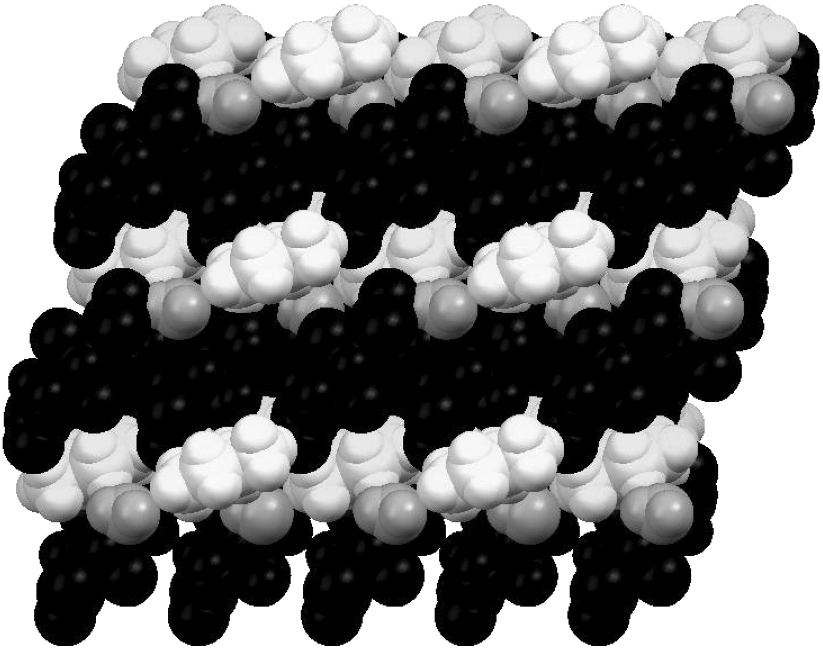

Figure 3: Crystal packing of **1**; anions are black, cations are white, and water molecules are gray.

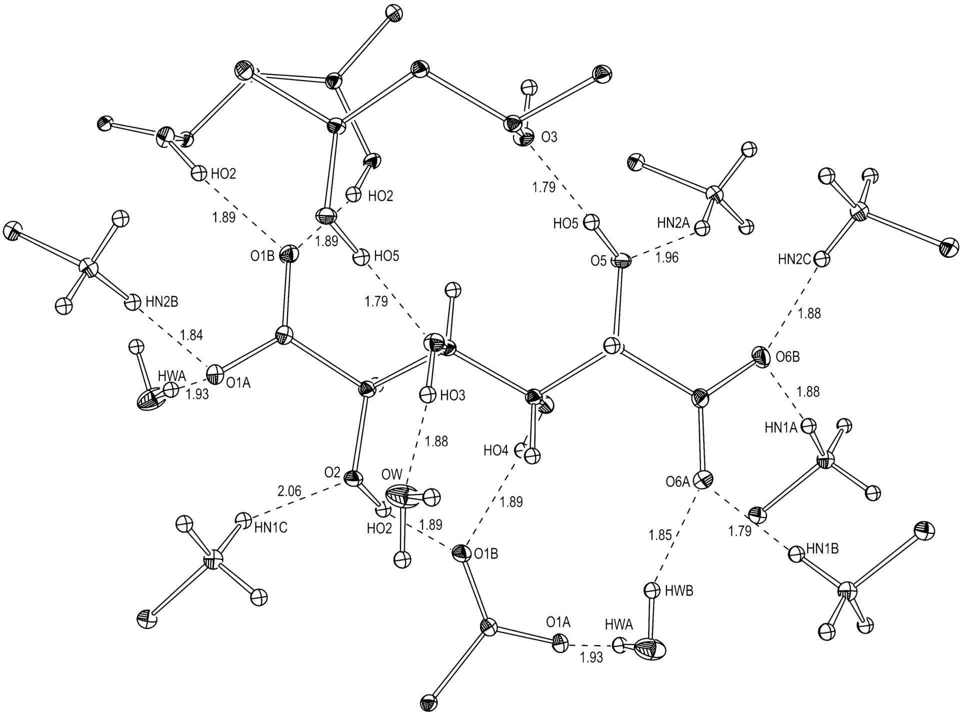

Figure 4: H-bonding interactions in **1**.

The water molecule in the lattice links three anions by acting as an H-bond donor to two different carboxylate O atoms, and as an acceptor from a C-O-H3, all three bonds being relatively short (H. . . O distances of 1.85–1.93 Å).

Both oxygen atoms of the C1 carboxylate group act as multiple H-bond acceptors, from two different C-O-H groups in the same anion for O1b and from one N-H group and from the water molecule for O1a. C-O-H2 and C-O-H3 are involved in cooperative bonding, acting as a donor to an O^- and an acceptor from an $-NH_3^+$ for the former, while the latter has stronger interactions as a donor to the water molecule and an acceptor from an adjacent C-O-H5. C-O-H4 is just involved in a single donor interaction to an O^-, while C-O-H5 has cooperative bonding as both an acceptor (from N-H) and donor (to –OH3). Finally, the C6 carboxylate oxygen atoms are acceptors from two donors, two N-H for O6b (with a possible much weaker interaction with a third $-NH_3^+$) and from an $-NH_3^+$ and the H_2O for O6a.

Despite the extensive network, and the formal charge separation that might have been expected to enhance the H-bonding, the density of this salt at 1.486 g cm^{-3} is much lower than that of galactaric acid itself, 1.790 g cm^{-3}. The extensive H-bonding network does, however, support the observation of poor solubility in water for this salt.

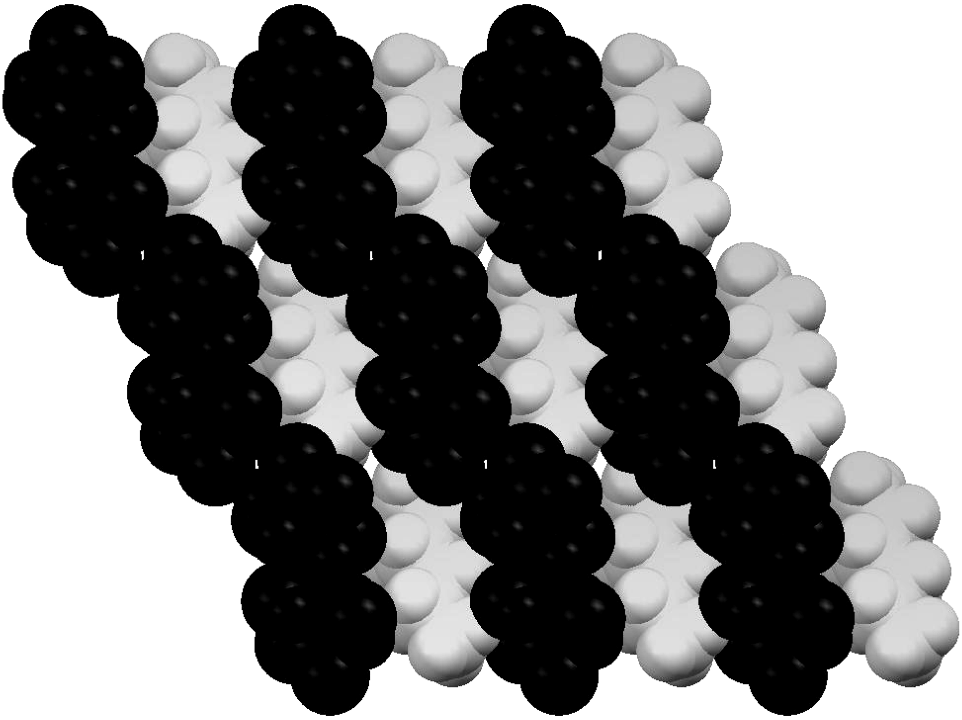

Figure 5: Crystal packing of **2**; anions are black and cations are white.

H-bonding in tetramethylenediammonium galactarate, 2

The triclinic unit cell contains one cation and one anion, each lying on an inversion center. Both are in the fully extended conformation, and the packing leads to stacked alternating layers of cations and anions (Fig. 5). Because of the higher symmetry, and the absence of water molecules in the lattice, the hydrogen bonding is simpler to analyze (Fig. 6).

Once again all three –NH_3^+ hydrogens are involved as donors, forming two H-bonds directly to O^- groups and one indirectly via a cooperative N-H. . . O-H. . . O^- motif involving C-O-H3 (Fig. 5). O1b of the carboxylate participates in two strong H-bonds, one from an N-H and one from O-H3. O1a forms one short N-H. . . O^- link, a weaker intermolecular one to an adjacent C-O-H2, and an intramolecular one to its own C-O-H2.

As described above, C-O-H2 provides a bifurcated intramolecular H-bond to an O1a and an intermolecular one to O1a, both weak, while C-O-H3 is involved cooperatively as described above. Despite the increased organic component of the cation compared to that in **1**, the density is greater at 1.523 g cm^{-3} and, unlike **1**, **2** is soluble in water.

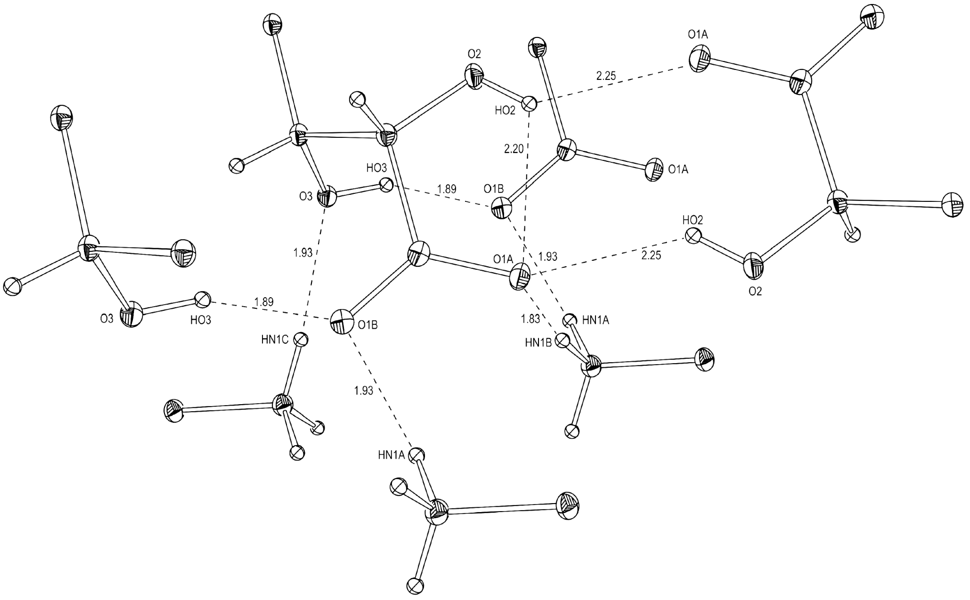

Figure 6: H-bonding interactions in **2**.

H-bonding in 3′,6′-dioxaoctamethylenediammonium galactarate, ***3***

Despite the extra oxygen atoms in the cation, this salt has the lowest density of all of the structures discussed here, 1.426 g cm^{-3}; this salt is extremely soluble in both water and methanol. The unit cell contains one cation and one anion, both lying on inversion centers, and two water molecules. The central part of the cation is in an extended conformation, but the ammonium groups are rotated to a gauche configuration (N1-C4-C5-O5 torsion angle 60.76°(10)) (Fig. 7).

The galactarate anions are lined up head to tail in a planar array (Fig. 8) held by reciprocal C-O-H2…O1a^{-}, and C-O-H3…O1b^{-}interactions (Fig. 9).

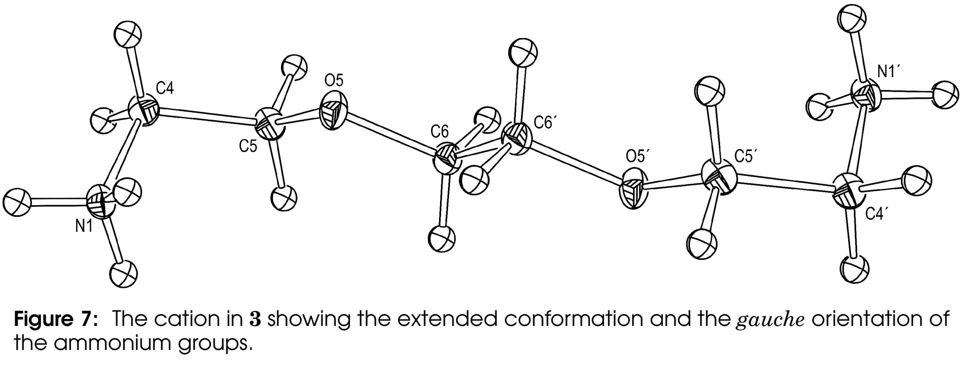

Figure 7: The cation in **3** showing the extended conformation and the *gauche* orientation of the ammonium groups.

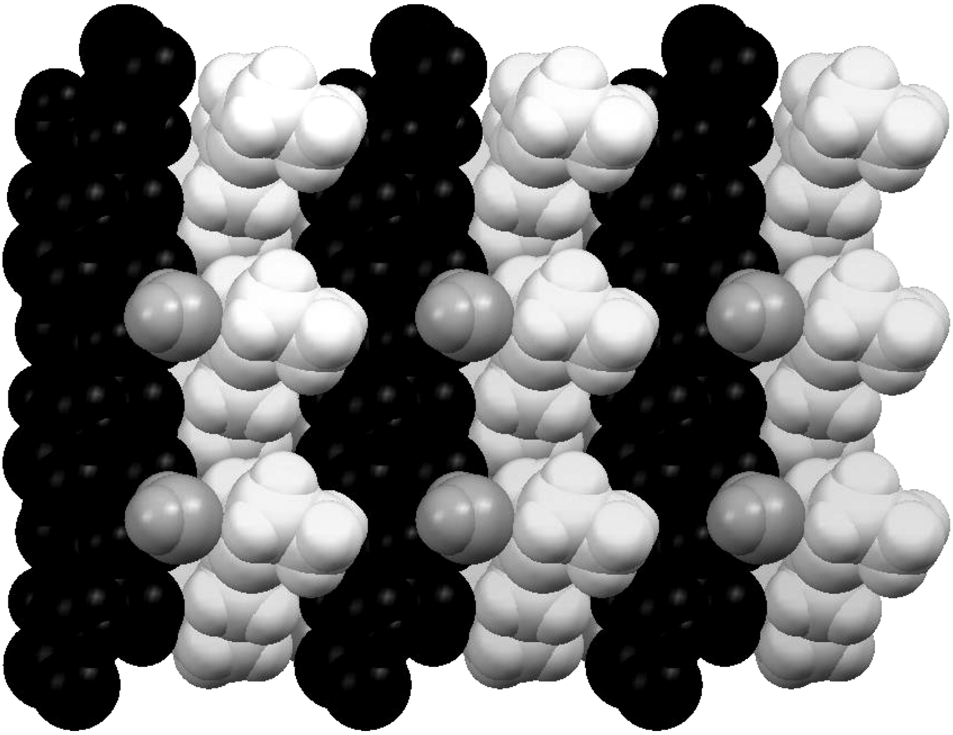

Figure 8: Crystal packing of **3**; anions are black, cations are white, and water molecules are gray.

These arrays are cross-linked by the cations and the H_2O molecule. The $–NH_3^+$ acts as a donor to the H_2O, to one O^- and to the oxygen of the OH group on C3. As with **2**, O1a, C1, C2, and O2 are coplanar, allowing an intramolecular O2-H2… O1a link. The carboxylate O^- act as acceptors from N-H and C-O-H2 for O1a and from H_2O and C-O-H3 for O1b. The O atoms of the OH groups on C2 and C3 are acting as both donors and acceptors in each case. The ether O atoms of the cation are not involved at all with any of the hydrogen bonding. This salt is also soluble in water.

H-bonding in m-xylylenediammonium galactarate, 4

This salt also crystallizes with a triclinic unit cell, the asymmetric unit containing a complete cation, two water molecules, and two half-anions lying on different inversion centers leading to two crystallographically distinct galactarate units. The first galactarate packs with one of the water molecules to generate a planar array perpendicular to the c-axis, with the other galactarate, the cation, and the other water molecule sandwiched between the layers in alternating positions (Fig. 10).

For the *m*-xylylenediammonium cation, the two diammonium groups are on opposite faces of the benzene ring; since the C16-C11-C17-N17 torsion angle

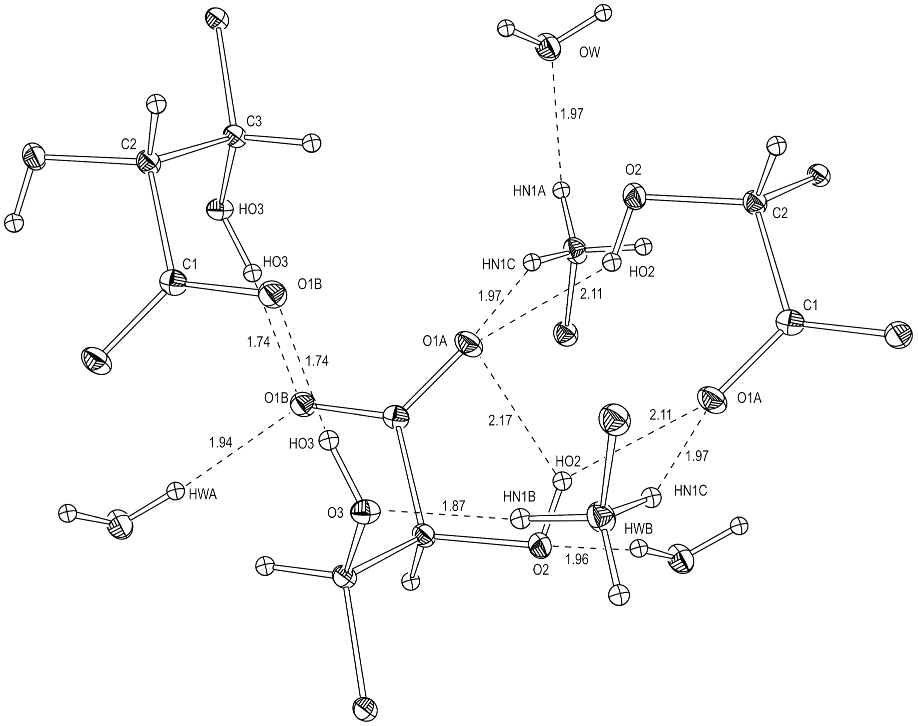

Figure 9: H-bonding interactions in **3**.

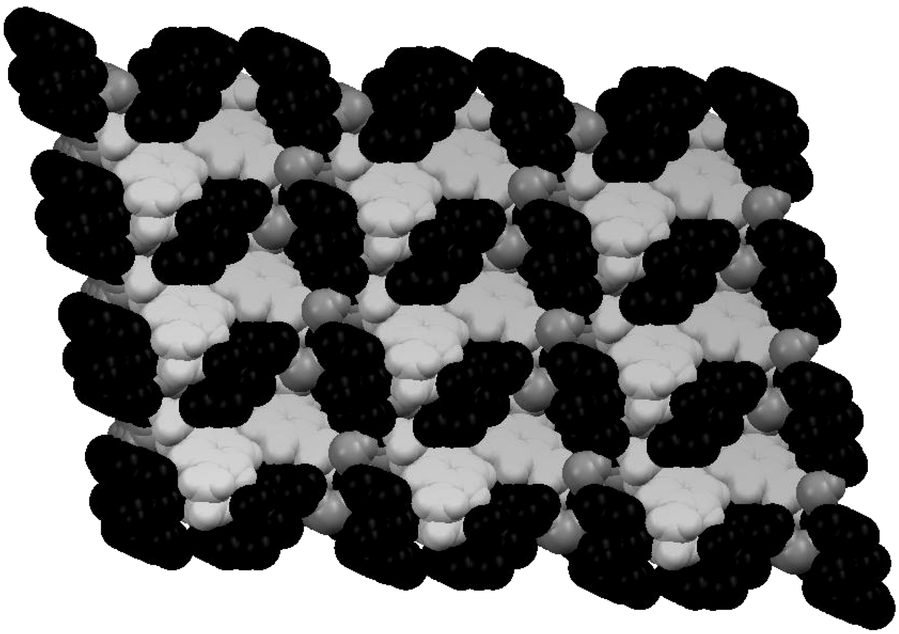

Figure 10: Crystal packing of **4**; anions are black, cations are white, and water molecules are gray.

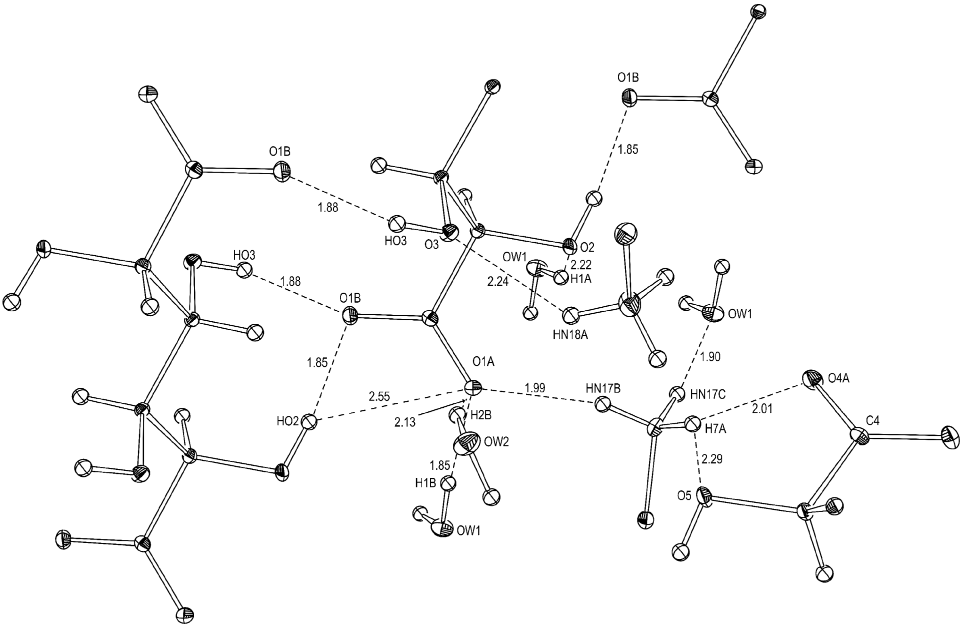

Figure 11: H-bonding interactions in the first galactarate unit of **4**.

is 62.00(11)° and the C14-C15-C18-N18 torsion angle is 71.74(12)°, this puts one hydrogen atom on both methylene units in the plane of the benzene ring and the other hydrogens at 57.62(86)° for H17B and 47.67(93)° for H18A from the plane. This conformation is seen in other *m*-xylylenediammonium salts.[17]

With two crystallographically distinct galactarate anions and two water molecules, **4** has the largest number of hydrogen bonds to describe and Figures 11 and 12 show the hydrogen bonding of the first and second galactarate units, respectively.

Neither of the two independent galactarate anions associates directly with the other, each only interacting with the water molecules, the ammonium groups, or the galactarate groups of the same designation. For the first anion O1a is involved in three hydrogen bonds from –NH_3^+ and from both H_2Os, and O1b has two from the hydroxyl groups on C2 and C3′ of a symmetry-related galactarate in a reciprocal arrangement. Both C2 and C3 hydroxyl oxygens are acceptors from H_2O and –NH_3^+, respectively.

For the second galactarate O4a is involved in two hydrogen bonds from H_2O and NH_3^+, while O4b is involved in two hydrogen bonds from the C-OHs on the C5 and C6′ atoms of the same adjacent galactarate. Both of these hydroxyl oxygens also accept a weak bifurcated hydrogen bond from an N-H of the cation. The majority of the water hydrogen bonding is to the first galactarate unit with only one hydrogen bond from a water molecule to the second galactarate. The final hydrogen bonds involve the ammonium protons and the

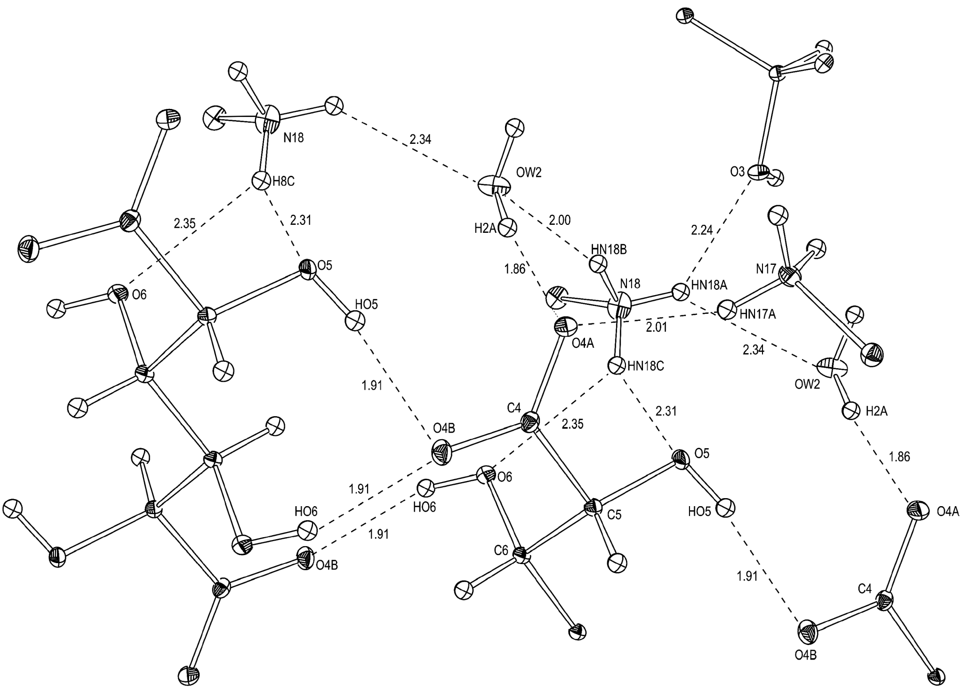

Figure 12: H-bonding interactions of the second galactarate unit of **4**.

water oxygens. The hydrogen bonding in **4** is weak compared to the rest of the examples, with only 8 of the 20 hydrogen bonds under 2 Å. This accounts for the low density of 1.469 g cm^{-3}. Nevertheless, this salt is insoluble in water, possibly because of the bulky nonpolar portion of the cation.

*H-bonding in 1,4-cyclohexyldiammonium galactarate, **5***

This crystal structure has two cations and two anions in the monoclinic unit cell, each lying on an inversion center. More than any of the others discussed here, this one consists of alternating cations and anions in an 8:8 coordination (Fig. 13) reminiscent of the classic CsCl ionic structure. There is only one unique H-bond directly linking galactarate units. The H-bonding network is the most straightforward (Fig. 14). Again, all three of the $-NH_3^+$ hydrogen atoms act as donors, in this case to O^- of the carboxylate groups of three different galactarates. $O1a^-$ accepts H-bonding from an NH_3^+ and from a C-O-H3 of a neighboring galactarate, while $O1b^-$ has two interactions with different $-NH_3^+$ units together with an intramolecular interaction from C-O-H2. These are the only interactions for the OH groups on C2 and C3. Although the network is relatively simple, it obviously provides for efficient packing, since the density is the highest of all five examples at 1.526 g cm^{-3}. This salt was poorly soluble in water but sufficiently dissolved for NMR analysis.

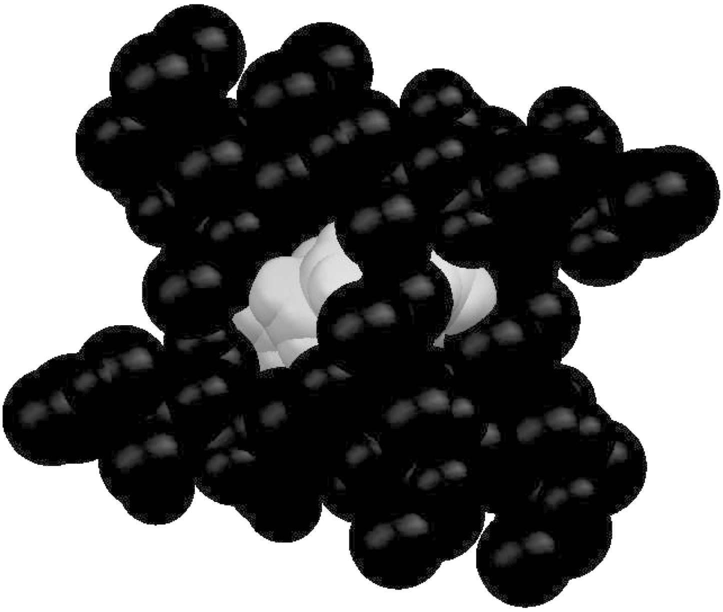

Figure 13: Crystal packing of **5** showing the cation surrounded by eight anions; anions are black and cations are white.

Summary

From the five examples discussed, here some general conclusions can be drawn about the hydrogen bonding interactions possible in these diammonium galactarates:

(i) The packing of the anions and cations is not at all predictable. Only for the cyclohexyldiammonium salt, **5**, is the crystal generated by essentially alternating cations and anions, which might have been intuitively expected for an ionic solid. In the other cases extensive anion-anion interactions are found in addition to cation-anion ones. This leads to alternating layers of anions and cations. This indicates that in the resultant polymers there may be an association between galactaryl units, which will influence the three-dimensional structure and physical properties.

(ii) The $-NH_3^+$ groups are very strong H-bond donors, all three hydrogen atoms always being involved in interactions with oxygen acceptors.

(iii) The $-COO^-$ oxygen atoms are good acceptors, always accepting at least two H-bonds from either the $-NH_3^+$ groups or from C-OH groups of adjacent galactarates. In three of the examples, **2**, **3**, and **5**, the conformation adopted by the carboxylate end of the galactarates allows an extra intramolecular H-bond between one of the carboxylate O^- and the –OH on C2, in addition to the two other H-bonds.

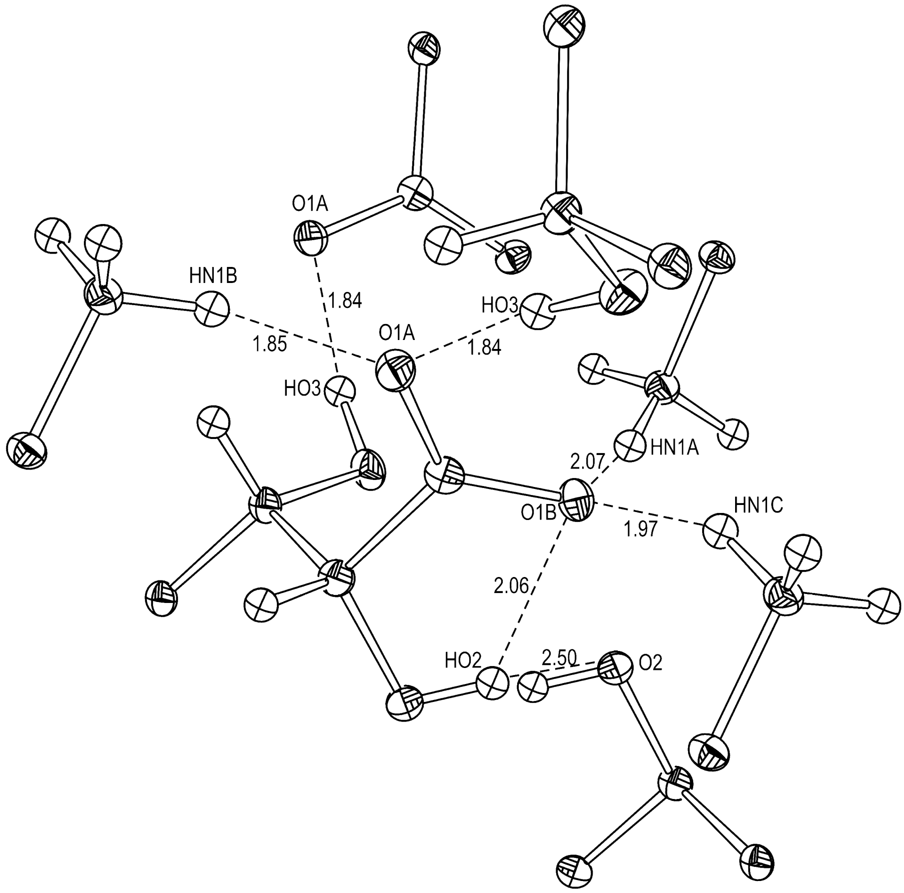

Figure 14: H-bonding interactions in **5**.

(iv) The relative packing efficiencies, and consequent densities, do not seem to follow any obvious trend. Table 2 summarizes the densities and volume per non-H atom for each of the salts and for galactaric acid.

From these it is clear that the packing is reasonably efficient for all examples, since a volume of about 18 Å^3/atom is usually accepted as average for organic structures, but that galactaric acid is exceptionally closely packed in the crystal. It is noticeable that the two most dense examples among the salts are those that do not incorporate water molecules in the lattice. This may indicate good packing between the ions for **2** and **5**, so that extra H_2O is not needed to occupy gaps, or it may be that the directionality of the H-bonding involving the water molecules in **1**, **3**, and **4** expands the lattice to give a less dense crystal, as is well known for ice itself.

For the bulk polymers these crystal structures may be a better guide to packing than solution conformation, in which interactions with the solvent may occur, with the reservation that, of course, the polymer does not contain

Table 2: Comparison of packing efficiency in **1–5**, galactaric acid, and ammonium galactarate.

Compound	Crystal density (g cm^{-3})	Non-H atom volume (Å^3 atom^{-1})
Galactaric acid[a]	1.790	13.8
$(NH_4^+)_2$ galactarate[b]	1.624	15.6
1	1.486	17.0
2	1.523	16.3
3	1.426	17.6
4	1.469	16.6
5	1.526	16.0

[a] Taken from reference 3.
[b] Taken from reference 6.

ions, so that the H-bonding network is unlikely to duplicate exactly those described here. However, H-bonding is still possible between $–NH_2$ and –COOH units, and thus it seems likely that the galactaryl unit will be always in the extended conformation and that in the bulk polymers it is likely that alternating layers of galactaryl and alkyl moieties will occur.

Supplementary Information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 701076-701080, for compounds **1–5**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.ac.uk). Supplementary tables give the parameters for the H-bonding in **1–5**.

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