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Molecular Packing and Hydrogen Bonding in the Crystal Structures of the *N*-(*n*-Alkyl)-*D*-gluconamide and the 1-Deoxy-(*N*-methyl-alkanamido)-*D*-glucitol Mesogens

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Despite differences in molecular configuration and crystal symmetry, the crystal structures of the odd and even alkyl chain members of the *N*-(*n*-alkyl-*D*-gluconamides and the odd alkyl chain members of the 1-deoxy-(*N*-methyl alkanamido)-*D*-glucitols have closely related hydrogen-bond systems, which include a *homodromic* four-bond cycle. This is associated with the monolayer head-to-tail molecular packing common to these crystal structures.

INTRODUCTION

Amphiphilic molecules in which a hydrocarbon chain is linked to a pyranose or an alditol moiety have received attention in recent years because of their use as non-ionic surfactants for crystallizing membrane proteins.[1,2] All these molecules with more than six carbon atoms in the alkyl chain form thermotropic liquid crystals[3] and the more soluble form lyotropic liquid crystals[4] and gels.[5,6]

Seven crystal structures of the alditol derivatives have been reported:

N(*n*-alkyl)-*D*-gluconamides, **I**, with $n = 6, 7, 9, 10$,

I $CH_3(CH_2)_nNH{\cdot}CO{\cdot}(CHOH)_4CH_2OH$[7–10]

1-deoxy-(*n*-methyl alkanamido)-*D*-glucitols, **II**†, with $n = 6$, 7 and 9,

II $CH_3(CH_2)_nCO{\cdot}NH(CH_3){\cdot}CH_2{\cdot}(CHOH)_4CH_2OH$[11,12]

†These compounds are also named MEGA-*n*; *N*-*D*-gluco-*N*-methyl alkanamides,[2] or alkanoyl-*N*-methyl glucamides.[11]

As with the fatty acids,[13] the compounds with odd and even carbon atoms in the alkyl chains have different crystal structures. **I** with $n = 6$ and 10 are triclinic, P1; **I** with $n = 7$ and 9 are monoclinic, $P2_1$; **II** with $n = 6$ (MEGA-8) is orthorhombic, $P2_12_12_1$; **II** with $n = 7$ (MEGA-9) and $n = 9$ (MEGA-11) are triclinic, P1.

The crystal structures of **I** have monolayer head-to-tail molecular packing irrespective of whether they are in the odd or even series. The crystal structures of **II** have this packing only with the odd number of alkyl carbon atoms. In the even series of **II**, the molecular packing is bilayer head-to-head.[12] This is the molecular packing that has hitherto been observed without exception in the *n*-alkyl 1-O and 1-S *D*-pyranosides.[3,14–18]

The monolayer head-to-tail packing is unusual with amphiphilic molecules such as the cholesteric fatty acids[19] and the triacetyl springosine and alkyl glycerophosphocholines.[20] It is also unexpected in view of the observation that these crystals undergo thermotropic transitions to smectic A liquid crystals with *d*-spacings indicative of bilayer molecular clusters.[12]

Despite the differences in molecular configuration and crystal symmetry, these crystal structures have closely related hydrogen bond systems which are examined in this paper.

THE HYDROGEN BONDING

All six crystal structures referred to in Table I have monolayer head-to-tail packing with a common hydrogen bonding feature. This is a *homodromic* cycle[22] of strong bonds linking the hydroxyls O(3)H, O(4)H, O(5)H and O(6)H. As shown in Table I, the sequential character of the hydrogen bonding is retained, but reversed between the alkyl gluconamides and *N*-methyl alkanamido-glucitols.

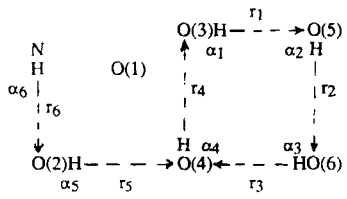
In compound **1**, the hydrogens on O(2)H, O(4)H and O(5)H were not located, neither were those on O(2)H in compound **2** nor those on O(2)H and O(5)H in compound **3**, but the O- - -O separations (in parentheses) are consistent with hydrogen bond formation. In crystal structures **1–4**, there are O(2)H- - -O(4) intramolecular hydrogen bonds which stabilize the straight-chain alditol conformation.[23] There is also a separate intermolecular N—H- - -O=C hydrogen bond. In crystal structures **5** and **6**, the amide nitrogen is methyl substituted and the hydroxyl O(2)H forms a hydrogen bond to the carbonyl oxygen O(7). O(2) is then linked to the homodromic cycle by means of a three-center bond from O(3)H.

Cyclic hydrogen bond systems, including homodromic cycles, are observed in the crystal structures of the cyclodextrin hydrates.[24] They are never observed in the crystal structures of the alditols, where infinite chains are the rule.[23] Because of the cooperativity of sequential hydrogen bonding,[21,25] homodromic cycles are energetically the more stable of the various cyclic systems.[26] In *D*-galactaric acid (mucic acid), a four-link homodromic cycle together with a carboxylic dimer hydrogen bond system is responsible for the unusual insolubility of this polyhydroxy acid in cold water.[27]

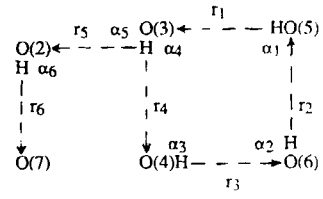
We believe therefore that that monolayer head-to-tail molecular packing, *per se*, is intrinsically less energetically favorable than the more common bilayer head-

TABLE I

Hydrogen bond distances and angles in the monolayer head-to-tail crystal structures of the N-(n-alkyl)-gluconamide and the 1-deoxy-(N-methyl alkanamido)-D-glucitols



1, 2, 3, 4



5, 6

1: N-(n-heptyl)-D-gluconamide[9]

2: N-(n-octyl)-D-gluconamide[7,8]

3: N-(n-decyl)-D-gluconamide[9]

4: N-(n-undecyl)-D-gluconamide[10]

5: 1-deoxy-(N-methyl nonamido)-D-glucitol (MEGA-9)[11]

6: 1-deoxy-(N-methyl undecanamido)-D-glucitol (MEGA-11)[12]

	1	2	3	4	5	6
Bond lengths (Å)						
r_1	1.86	1.98	1.94	1.83	2.08	1.90
r_2	(2.83)	1.89	(2.72)	1.78	1.79	1.81
r_3	1.92	1.88	1.94	1.77	1.95	1.81
r_4	(2.86)	1.76	1.79	1.75	1.78	1.83
r_5*	(2.87)	(3.04)	(3.05)	2.01	2.40	2.46
r_6*	2.10	2.22	2.18	2.20	2.30	1.93
N---H- - -O(1)=C	2.10	2.17	2.09	2.21		
Bond angles (deg)						
α_1	141	143	140	159	123	146
α_2	-	162	-	171	166	164
α_3	134	148	144	177	165	160
α_4	-	171	175	171	154	159
α_5*	-	-		179	99	98
α_6*	105	109	112	108	131	156
N—H- - -O=C	140	148	143	86	-	-

All O—H and N—H bond lengths have been normalized to 0.97 and 1.00 Å respectively to correct for the bonding electron density distribution.[21] Values in parentheses are O---O separations when hydrogen coordinates are not available. Asterisks indicate intramolecular bonds. E.s.d.s for hydrogen bond lengths are ≈0.05 Å, for O---O separations ~0.005 Å.

to-head packing, but the extra stability comes from the possibility of forming this type of strong cooperative hydrogen bonding. On heating the crystals, the hydrogen bonding is weakened by the increase in the vibrational and oscillational thermal motion of the O—H bonds. In consequence, transitions take place, either to the bilayer smectic A liquid crystal phase or another bilayer crystalline phase which preceeds the liquid crystal phase, as has been shown by X-ray diffraction to occur in the *N*-(*n*-undecyl)-*D*-gluconamide crystal structure.[10]

This greater sensitivity to thermal motion of hydrogen-bonding *vis-a-vis* the alkyl chain van der Waals packing provides an explanation for the observation that in these series of compounds and in the alkyl *D*-glucopyranosides, the transition temperatures from crystal to liquid crystal are nearly independent of alkyl chain length, whereas the transition temperatures from liquid crystal to isotropic liquid increases regularly with chain length.[28,29] This implies that on heating, the rupture from the crystal lattice to the molecular clusters takes place between the hydrogen-bonded carbohydrate moieties. The *core* of the liquid crystal cluster is therefore the intercalated alkyl chains, not the hydrogen bonded carbohydrate moieties as previously inferred.[30] Similar observations and conclusions have been made from a study of the thermotropic properties of homologous series of *n*-alkyl 1-*S*-α-*D*-glucopyranosides[31] and aldose dialkyl dithioacetals.[32]

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NOTE ADDED IN PROOF:

In the crystal structure of *N*-(*n*-decyl)-*D*-ribonamide [B. Tinant, J. P. Declercq and M. van Meerssche, *Acta Crystallogr.*, **C42**, 579–581 (1986)], the monolayer head-to-tail molecular packing is also associated with a homodromic cycle of four strong hydrogen bonds linking O(2)H—O(4)H—O(5)H—O(3)H.