Supramolecular structures of substituted α,α'-trehalose derivatives

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The structures of five substituted α,α'-trehalose trehalose derivatives have been determined, and these are compared with those of four previously published analogues. In 2,2′,3,3′,4,4′-hexaacetato-6,6′-bis-O-methylsulfonyl-α,α'-treha-lose, $C_{26}H_{38}O_{21}S_2$, where the molecules lie across twofold rotation axes in the space group $C2$, a single $C-H\cdots O{=}S$ hydrogen bond links the molecules into sheets. 2,2′,3,3′,4,-4′-Hexaacetato-6,6′-bis-O-(4-toluenesulfonyl)-α,α'-trehalose, $C_{38}H_{46}O_{21}S_2$, crystallizes with $Z' = 2$ in the space group $P2_12_12_1$ and a combination of three $C-H\cdots O$ hydrogen bonds, each having a carbonyl O atom as an acceptor, and a $C-H\cdots\pi$(arene) hydrogen bond link the molecules into a three-dimensional framework. 2,2′,3,3′,4,4′-Hexaacetato-6,6′-diazido-α,α'-trehalose, $C_{24}H_{32}N_6O_{15}$, crystallizes as a partial ethanol solvate and three $C-H\cdots O$ hydrogen bonds link the substituted trehalose molecules into a three-dimensional framework. In 2,2′,3,3′-tetraacetato-6,6′-bis(N-acetylamino)-α,α'-trehalose dihydrate, $C_{24}H_{36}N_2O_{15}\cdot 2H_2O$, the substituted trehalose molecules lie across twofold rotation axes in the space group $P2_12_12$ and a three-dimensional framework is generated by the combination of $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds. The diaminotrehalose molecules in 6,6′-diamino-α,α'-trehalose dihydrate, $C_{12}H_{24}N_2O_9.2(H_2O)$, lie across twofold rotation axes in the space group $P4_32_12$: a single $O-H\cdots N$ hydrogen bond links the trehalose molecules into sheets, which are linked into a three-dimensional framework by $O-H\cdots O$ hydrogen bonds.

1. Introduction

Recent reports on the structures of the multiply substituted α,α'-trehalose derivatives (1) [see (I)], which crystallizes as an ethyl acetate monosolvate (Baddeley *et al.*, 2001), (2), which crystallizes as a partial (0.7 mol) hydrate (Clow *et al.*, 2001), (3) (Baddeley *et al.*, 2002) and (4) (Baddeley *et al.*, 2003) indicate that, despite the wide variation of the substituents, particularly those at the 6 and 6′ positions, the pyranose rings all adopt very similar chair conformations, as judged by the ring-puck-ering parameters (Cremer & Pople, 1975).

In (1)–(3) there are no direction-specific interactions between the molecules, but in (4) a single $O-H\cdots O$ hydrogen bond links the molecules into helical C12 (Bernstein *et al.*, 1995) chains, which are weakly reinforced by a $C-H\cdots O{=}C$ hydrogen bond. Two further $C-H\cdots O$ contacts were reported in (4), but both of these involve methyl $C-H$ bonds. Since it is now well established (Riddell & Rogerson, 1996, 1997) that in the solid state methyl groups, H_3C-X, generally undergo very rapid rotation about their $C-X$ bonds, even at

very low temperatures, such that the H-atom sites identified from diffraction data generally represent the minima in the corresponding rotational potential functions, rather than statically occupied sites, it is unlikely that contacts involving methyl C—H bonds such as those reported will, or can, have any structural significance.
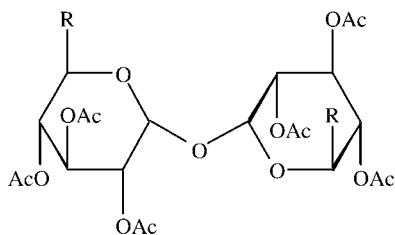
(1) R = CH$_2$OCOMe
(2) R = CH$_2$OCOCHMe$_2$
(3) R = CH$_2$OCPh$_3$
(5) R = CH$_2$OSO$_2$Me
(6) R = CH$_2$OSO$_2$C$_6$H$_4$Me
(7) R = CH$_2$N$_3$
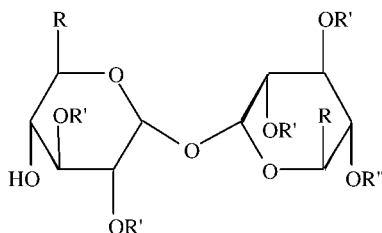
(4) R = CH$_2$OCOCMe$_3$; R' = R" = COCMe$_3$
(8) R = CH$_2$NHCOMe; R' = COMe; R" = H
(9) R = CH$_2$N$_3$; R' = R" = H

(I)

In this paper, we report the molecular and supramolecular structures of further examples of substituted α,α'-trehalose derivatives, (5)–(9) [see (I)], where the substituents were selected to afford the possibility of other types of direction-specific intermolecular interactions: for example, (5) and (6) both offer the possibility of C—H···O=S hydrogen bonds, while both C—H···π(arene) hydrogen bonds and aromatic π···π stacking interactions could occur in (6); C—H···N hydrogen bonds could in principle occur in (7); O—H···O and N—H···O hydrogen bonds could both occur in (8); and O—H···O, N—H···O, and O—H···N hydrogen bonds are all possible in (9).

2. Experimental

2.1. Syntheses

Compound (5): A solution of 2,2',3,3',4,4'-hexa-O-acetyl-α,α'-trehalose (10 g, 16.8 mmol) and methanesulfonyl chloride (5.8 g, 4 cm^3, 50.5 mmol) in acetonitrile (30 cm^3) and pyridine (10 cm^3) was stirred for 3 h, and rotary evaporated to leave an oily solid. After shaking the residue with water, a solid was

collected, washed with water, dried *in vacuo* at 330 K and recrystallized from ethanol; yield 10.4 g (92%), m.p. 441 K, lit. m.p. 441–442 K; (Birch & Richardson, 1968); $[\alpha]_D$ (CHCl$_3$) 146.2°, lit. $[\alpha]_D$ (CHCl$_3$) 143° (Birch & Richardson, 1968). NMR (CDCl$_3$): $\delta(^1$H) 2.01 (s, 3H, Me), 2.05 (s, 3H, Me), 2.08 (3, 3H, Me), 3.01 (s, 3H, Me), 4.11 (td, 1H, J = 2.14, 6.22, H-5), 4.14 (dd, 1H, J = 2.14, 11.10, H-6'), 4.22 (dd, 1H, J = 6.22, 11.10, H-6), 4.98 (t, 1H, J = *ca* 9), 5.01 (dd, 1H, J = 3.85, 10.37, H-2), 5.28 (d, 1H, J = 3.85, H-1), 5.46 (t, 1H, J = 10.37, H-3): $\delta(^{13}$C) 20.6, 37.7, 66.5, 68.2, 68.4, 69.6, 69.7, 92.6, 169.6, 169.8, 169.9. IR (KBr, cm^{-1}): 2972, 2932, 1760, 1743, 1357, 1219, 1178, 1143, 1037, 1018, 989, 955, 811.

Compound (6): A solution of 2,2',3,3',4,4'-hexa-O-acetyl-α,α'-trehalose (10 g, 16.8 mmol) and 4-toluenesulfonyl chloride (9.6 g, 50.5 mmol) in acetonitrile (30 cm^3) and pyridine (10 cm^3) was stirred for 24 h and DMAP (*ca* 10 mg) added. After stirring for a further 5 h, the solution was evaporated to a syrupy residue, which was poured into water with vigorous stirring. The off-white precipitate was filtered off, washed with water and air dried. The resulting solid was washed with boiling ethanol, dried at 330 K in vacuum and recrystallized from ethanol; yield 11.4 g (90.4%), m.p. 431–434 K, lit. m.p. 443–445 K (Birch & Richardson, 1968). NMR (CDCl$_3$): $\delta(^1$H) 1.98 (s, 3H, Me), 2.01 (s, 3H, Me), 2.06 (s, 3H, Me), 2.43 (s, 3H, Me), 4.02 (m, 2H), 4.10 (m, 1H), 4.90 (m, 3H), 5.38 (m, 1H), 7.32 (d, 2H, J = 7.95), 7.72 (d, 2H, J = 8.35): $\delta(^{13}$C) 20.6, 21.6, 67.6, 68.2, 68.6, 69.2, 69.8, 92.8, 128.0, 129.9, 132.4, 145.3, 169.5, 169.6, 169.9. IR (KBr, cm^{-1}): 2963, 1754, 1371, 1221, 1178, 1081, 1039, 979, (810, 669, 554). MS (ES$^+$, MeCN): 667.4 [100%], 796.4 [30%], 925.5 [20%, M + Na], 458.4 [18%], 417.4 [15%], 771.5 [10%, M − CH$_3$C$_6$H$_4$SO$_2$ + Na].

Compound (7): To a solution of 2,2',3,3',4,4'-hexa-O-acetyl-6,6'-di-O-methanesulfonyl-α,α'-trehalose (10.0 g, 14.9 mmol) in DMSO (60 cm^3) was added sodium azide (3.0 g, 46 mmol) and the solution heated to 350 K. After 1 h, TLC with ethyl acetate:light petroleum (boiling range 313–333 K) (2:1 v/v) as eluent showed complete reaction. The solution was poured into water (200 cm^3) and the solid was collected, dried and recrystallized from ethanol as a partial solvate; yield 8.5 g (94%), m.p. 413 K, lit. m.p. 387–389 K (Birch & Richardson, 1968), 392–393 K (Kurita *et al.*, 1994), 394–398 K (Liav & Goren, 1980); $[\alpha]_D$ (CHCl$_3$) 127°, lit. $[\alpha]_D$ (CHCl$_3$) 134° (Birch & Richardson, 1968), (CHCl$_3$) 138° (Kurita *et al.*, 1994). NMR (CDCl$_3$): $\delta(^1$H) 2.02 (s, 3H, Me), 2.05 (s, 3H, Me), 2.11 (s, 3H, Me), 3.16 (dd, 1H, J = 2.44, 13.32, H-6'), 3.36 (dd, 1H, J = 7.39, 13.32, H-6), 4.08 (m, 1H, J = 2.44, 7.39, 9.1, H-5), 4.98 (dd, 1H, 9.4, 9.9, H-4), 5.07 (dd, 1H, J = 3.82, 10.31, H-2), 5.31 (d, 1H, J = 3.82, H-1), 5.45 (dd, 1H, J = 9.4, 10.31, H-3): $\delta(^{13}$C) 20.7, 51.0, 67.7, 69.8, 69.9, 92.7, 169.6, 170.0. IR (KBr, cm^{-1}): 2101, 1740, 1211, 1033, 1014. MS (ES$^+$, MeCN): 667.2 [100%, M + Na], 105.1 [50%], 642.2 [20%].

Compound (8): To a solution of 2,2',3,3',4,4'-hexa-O-acetyl-6,6'-di-O-azido-α,α'-trehalose (10.0 g, 16.4 cm^3) in thf (80 cm^3) was added triphenylphosphine (9.0 g, 34.4 mmol) and water (2 cm^3). After stirring for 1 h, TLC, using ethyl acetate: light petroleum (2:1 v/v) as eluent, indicated the consumption of the starting material. The suspension was filtered and the solid

Table 1
Experimental details.

	(5)	(6)	(7)	(8)	(9)
Crystal data					
Chemical formula	$C_{26}H_{38}O_{21}S_2$	$C_{38}H_{46}O_{21}S_2$	$C_{24}H_{32}N_6O_{15}\cdot0.35C_2H_6O$	$C_{24}H_{36}N_2O_{15}\cdot2H_2O$	$C_{12}H_{24}N_2O_9\cdot2H_2O$
M_r	750.68	902.89	660.68	628.58	376.36
Cell setting, space group	Monoclinic, $C2$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12$	Tetragonal, $P4_32_12$
a, b, c (Å)	21.3279 (8), 8.9299 (4), 8.8382 (4)	18.1484 (9), 21.1046 (9), 23.4224 (14)	12.2281 (4), 15.5803 (6), 18.1066 (8)	8.8385 (2), 21.8363 (8), 8.0831 (2)	8.6093 (2), 8.6093 (2), 22.1566 (8)
β (°)	99.4537 (17)	90.00	90.00	90.00	90.00
V (Å^3)	1660.43 (12)	8971.1 (8)	3449.6 (2)	1560.04 (8)	1642.25 (8)
Z	2	8	4	2	4
D_x (Mg m^{-3})	1.501	1.337	1.272	1.338	1.522
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3048	14 269	4368	2067	1163
θ range (°)	3.3–27.5	3.0–24.4	3.1–27.5	2.5–27.5	3.0–27.5
μ (mm^{-1})	0.25	0.20	0.11	0.11	0.13
Temperature (K)	120 (2)	120 (2)	150 (2)	120 (2)	120 (2)
Crystal form, colour	Block, colourless	Lath, colourless	Block, colourless	Block, colourless	Block, colourless
Crystal size (mm)	$0.30 \times 0.25 \times 0.15$	$0.30 \times 0.10 \times 0.02$	$0.50 \times 0.30 \times 0.25$	$0.30 \times 0.20 \times 0.15$	$0.15 \times 0.15 \times 0.10$
Data collection					
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.934	0.949	0.942	0.960	0.972
T_{max}	0.964	0.996	0.974	0.983	0.987
No. of measured, independent and observed reflections	6104, 3048, 2781	34 701, 14 269, 8221	17 686, 4368, 2580	13 388, 2067, 1658	8561, 1163, 951
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.059	0.110	0.104	0.091	0.055
θ_{max} (°)	27.5	25.0	27.5	27.5	27.5
Range of h, k, l	$-27 \Rightarrow h \Rightarrow 26$	$-20 \Rightarrow h \Rightarrow 20$	$-12 \Rightarrow h \Rightarrow 15$	$-11 \Rightarrow h \Rightarrow 11$	$-9 \Rightarrow h \Rightarrow 11$
	$-10 \Rightarrow k \Rightarrow 11$	$-24 \Rightarrow k \Rightarrow 24$	$-18 \Rightarrow k \Rightarrow 20$	$-28 \Rightarrow k \Rightarrow 27$	$-11 \Rightarrow k \Rightarrow 11$
	$-11 \Rightarrow l \Rightarrow 11$	$-26 \Rightarrow l \Rightarrow 26$	$-23 \Rightarrow l \Rightarrow 23$	$-9 \Rightarrow l \Rightarrow 10$	$-20 \Rightarrow l \Rightarrow 28$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.145, 1.05	0.060, 0.136, 0.96	0.070, 0.191, 0.99	0.055, 0.148, 1.12	0.043, 0.126, 0.98
No. of reflections	3048	14 269	4368	2067	1163
No. of parameters	227	1113	439	215	115
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1014P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1153P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 0.0109P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.9377P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	0.001	<0.0001	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.62	0.86, −0.28	0.43, −0.43	0.47, −0.41	0.24, −0.35
Extinction method	$SHELXL$	None	None	None	None
Extinction coefficient	0.0065 (18)	–	–	–	–
Absolute structure	Flack (1983), 1018 Friedel pairs	Flack (1983), 6179 Friedel pairs	–	–	–
Flack parameter	0.16 (10)	−0.02 (8)	–	–	–

Computer programs used: *Kappa-CCD server software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *DENZO-SMN* and *SHELXS*97 (Sheldrick, 1997*b*), *SHELXL*97 (Sheldrick, 1997*a*), *PLATON* (Spek, 2003), *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

2,2′,3,3′,4,4′-hexa-*O*-acetyl-6,6′-diamino-6,6′-dideoxy-α,α′-tre-halose was washed with dichloromethane and dried; yield 4.9 g (51%), m.p. 418–428 K. NMR (CDCl$_3$): δ(^{1}H) 1.95 (s, 3H, Me), 2.05 (s, 3H, Me), 2.07 (s, 3H, Me), 3.14 (dd, 1H, *J* = 7.59, 14.15, H-6), 3.42 (t, 1H, *J* = 9.57, H-4), 3.68 (m, 1H, H-5), 3.81 (dd, 1H, *J* = 2.61, 14.15, H-6′), 4.85 (dd, 1H, *J* = 3.58, 10.3, H-2), 5.33 (d, 1H, *J* = 3.58, H-1), 5.34 (m, 1H, *J* = 10.3, H-3): δ(^{13}C) 21.3,

22.8, 40.8, 71.7, 72.0, 72.1, 72.4, 73.4, 94.4, 175.5. MS (ES$^+$): 579.0 [100%], 301.0 [80%], 615.1 [45%, *M* + Na].

A solution of the foregoing 2,2′,3,3′,4,4′-hexa-*O*-acetyl-6,6′-diamino-6,6′-dideoxy-α,α′-trehalose (0.5 g) in pyridine (10 cm^3) was allowed to stand overnight. Diethyl ether was added to precipitate the rearranged product, (8), which was recrystallized from aqueous ethanol as the dihydrate, m.p.

477 K; lit. m.p. (from ethanol/ether) 470–473 K (Liav & Goren, 1980); $[\alpha]_D$ (MeOH) 123.2°, lit. $[\alpha]_D$ (MeOH/water, 3:1) 130° (Liav & Goren, 1980). NMR (CDCl₃): $\delta(^1H)$ 1.80 (s, 3H, Me), 1.98 (s, 3H, Me), 2.02 (s, 3H, Me), 2.91 (m, 1H, H-6), 3.38 (t, 1H, J = 9.15, H-4), 3.54 (m, 1H, H-5), 3.70 (m, 1H, H-6'), 4.79 (dd, 1H, J = 3.66, 10.37, H-2), 5.18 (m, 2H, H-1 and H-3), 7.81 (t, J = 4.28, N*H*COCH₃): $\delta(^{13}C)$ 20.3, 20.8, 22.4, 69.0, 69.8, 71.4, 71.7, 90.6, 169.7, 169.9. IR (KBr, cm⁻¹): 3615–3096, 2867, 1739, 1643, 1571, 1437, 1378, 1236, 1141, 1047, 1017. MS (ES⁺): 615.3 [100%, M + Na], 573.3 [6%, M − Ac + Na], 1207.7 [2%, $2M$ + Na], 531.3 [1%, M − 2Ac + Na].

Compound (9): A suspension of 2,2′,3,3′,4,4′-hexa-*O*-acetyl-6,6′-di-*O*-azido-α,α'-trehalose (5.0 g, 7.8 mmol) and sodium methoxide (42.2 mg, 0.78 mmol) in methanol (40 cm³) was stirred for 4.5 h. The colourless solution was neutralized with DOWEX 50 W X-8 resin and the resin filtered off. The resin was washed with methanol, and the filtrates and washings were combined and evaporated to leave a white product, 6,6′-diazido-6,6′-dideoxy-α,α'-trehalose, which was crystallized from ethanol; yield 2.05 g (67%), m. p. 474–476 K; $[\alpha]_D$ (water) 153°; lit. m.p. 482–484 K (Birch & Richardson, 1968), 463–465 K (Kurita *et al.*, 1994), lit. $[\alpha]_D$ (water) 158° (Birch & Richardson, 1968). NMR (CDCl₃): $\delta(^1H)$ 3.29(t, 1H, J = 9.23, H-3/4), 3.39 (dd, 1H, J = 6.16, 13.68, H-6), 3.51 (m, 2H, J = 2.39, 13.68, H-6', H-2), 3.66 (t, 1*H*, J = 9.23, H-3/4), 3.81 (ddd, 1H, J = 2.39, 5.81, 9.92, H-5), 5.03 (d, 1H, J = 3.76, H-1): $\delta(^{13}C)$ 51.9, 71.5, 71.9, 72.1, 73.3, 94.8. IR (KBr, cm⁻¹): 3537–3263, 2947, 2918, 2200, 2106, 1601, 1446, 1415, 1344, 1288, 1147, 1105, 1070, 1043, 984, 930, 584, 567. MS (ES+): 415.1 ([100%, M + Na], 455.3 [32%], 432.9 [25%, M + Na + H₂O].

The foregoing 6,6′-diazido-6,6′-dideoxy-α,α'-trehalose (0.5 g, 1.27 mmol) and triphenylphosphine (1.34 g, 5.10 mmol) were dissolved in DMF (10 cm³). After 2 h when effervescence had ceased, ammonium hydroxide solution (30%, 4 cm³) was added and a precipitate formed. Ethanol (50 cm³) was added and the reaction mixture was heated at 330 K for 2 h to ensure complete dissolution. Crystals of 6,6′-diamino-6,6′-dideoxy-α,α'-trehalose dihydrate were obtained on cooling; 260 mg (60%); m.p. 498–500 K; lit. m.p. 473 K (Kurita *et al.*, 1994). NMR (CDCl₃): $\delta(^1H)$ 2.70 (dd, 1H, J = 7.63, 13.73, H-6), 2.95 (dd, 1H, J = 2.44, 13.73, H-6′), 3.29 (t, 1H, J = 9.77, H-3/4), 3.62 (dd, 1H, J = 3.36, 10.07, H-2), 3.71 (m, 1H, H-5), 3.80 (t, 1H, J = 9.77, H-3/4), 5.17 (d, 1H, J = 3.36, H-1)): $\delta(^{13}C)$ 44.0, 73.6, 73.8, 74.9, 75.0, 95.4. IR (KBr, cm⁻¹): 3544–3315, 2930, 2904, 1638, 1615, 1382, 1155, 1105, 1087, 1038, 1016, 986, 939.

2.2. Data collection, structure solution and refinement

Diffraction data for (5)–(9) were collected at 120 (2) K using a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997a,b; Spek, 2003).

Table 2
Ring-puckering parameters for pyranose rings (Å, °).

Ring-puckering parameters are for the atom sequence (O5, C1, C2, C3, C4, C5).

	Q (Å)	θ (°)	φ (°)
(1)	0.549 (2)	4.5 (3)	14 (3)
	0.563 (2)	4.3 (3)	106 (4)
(2)	0.56 (1)	9 (1)	94 (7)
	0.57 (1)	3 (1)	322 (21)
(3)	0.592 (2)	4.5 (2)	246 (2)
(4)	0.571 (5)	4.5 (5)	319 (5)
	0.568 (5)	5.5 (5)	317 (5)
(5)	0.579 (3)	4.9 (3)	122 (4)
(6)	0.553 (5)	3.9 (5)	11 (7)
	0.544 (5)	5.5 (5)	354 (5)
	0.554 (5)	6.3 (5)	357 (5)
	0.569 (5)	4.4 (5)	308 (7)
(7)	0.558 (4)	8.7 (4)	332 (3)
	0.546 (5)	5.1 (5)	347 (6)
(8)	0.567 (3)	8.4 (3)	75 (2)
(9)	0.580 (3)	4.3 (3)	245 (4)

For (5) the systematic absences permitted $C2$ and Cm as possible space groups: in view of the enantiopure nature of the chiral compound, the space group $C2$ was selected and confirmed by the analysis. For each of (6) and (7) the space group $P2_12_12_1$ was uniquely assigned from the systematic absences: similarly $P2_12_12$ was uniquely assigned for (8). For (9) the systematic absences permitted one of the enantiomeric pair $P4_12_12$ and $P4_32_12$: space group $P4_32_12$ was selected by reference to the known absolute configuration of the compound. The structures were all solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce the statistical bias (Wilson, 1976). In (5), (8) and (9) the disaccharide unit lies across a twofold rotation axis, while in (6) there are two independent disaccharide molecules in the asymmetric unit. In (7) there is a partially occupied ethanol: when the C and O atoms of this unit were refined isotropically, the site-occupancy factor refined to 0.35 (2). Thereafter this occupancy was fixed at 0.35, while the C and O atoms were refined anisotropically. In all the compounds the absolute structure was set from the known absolute configuration of the enantiopure chiral α,α'-trehalose starting material: in the case of (5) and (6) this was confirmed by the values of the Flack parameter (Flack, 1983), 0.16 (10) and −0.02 (8), respectively. For (7)–(9) the absence of any significant anomalous scatterers meant that the Flack parameters for these compounds [values 4.1 (18), −0.1 (17) and 0 (3), respectively] were inconclusive (Flack & Bernardinelli, 2000): hence the Friedel-equivalent reflections were merged prior to the final refinements of (7)–(9). All H atoms were located in difference maps and in (5)–(8) they were fully ordered. The H atoms bonded to C atoms were all treated as riding atoms with distances 0.95 Å

(aromatic), 0.98 Å (CH$_3$), 0.99 Å (CH$_2$) or 1.00 Å (aliphatic CH). The H atoms bonded to N or O in (8) were allowed to ride on their parent atoms at the positions found from the difference maps, with distances N—H 0.81 Å; O—H 0.82 Å (in the trehalose component) and 0.96 and 0.98 Å in the water molecule. In (9) the H atoms bonded to O2 and O4 in the trehalose component were both modelled as riding atoms using two sites with 0.50 occupancy and O—H distances of 0.84 Å; the H atoms bonded to N were allowed to ride at the positions found from the difference maps with N—H distances 0.95 and 1.00 Å; the H atoms of the water molecule were likewise allowed to ride at the positions found from the difference maps with O—H distances 0.94 and 0.99 Å. Examination of the refined structures using *PLATON* (Spek, 2003) showed small voids in (6), each of volume *ca* 37 Å^3; however, these contained no significant electron density as they are probably too small to accommodate even a water molecule.

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON*. The pyranose ring-puckering parameters are given in Table 2 and parameters for selected hydrogen bonds are given in Table 3.[1] Figs. 1–15 show the molecular aggregates, with the atom-labelling schemes, and aspects of the supramolecular structures.

3. Results and discussion

3.1. Pyranose ring conformations

For each of (5)–(9) the ring-puckering parameters for the pyranose rings, corresponding to the atom sequence (O5, C1, C2, C3, C4, C5) for each independent ring, are collected in Table 2, along with those for the previously published structures of (1)–(4) by way of comparison. It is clear that the gross conformations of these rings are largely independent both of the degree of substitution and of the steric bulk of the substituents. In every case the value of the parameter θ is less than 10°, indicating only a small distortion of the ring shape from the expected chair conformation; a regular chair conformer of exact $D_{3d}(\bar{3}m)$ symmetry has a θ value of zero (Boeyens, 1978).

Consistent with this deduction, the total puckering amplitude Q lies in the range 0.54–0.58 Å for (5)–(9), only a little less than the Q value of 0.63 Å calculated for the chair conformer of cyclohexane. However, the φ values in (5)–(9) are all close to $N \times 60°$, where N takes the values $N = 2$ in (5), $N = 0$, 5 or 6 in (6), $N = 6$ in (7), $N = 1$ in (8) and $N = 4$ in (9), indicating that the distortions from the chair conformation are all towards the boat conformation. Thus, the rings are slightly flattened, allowing the ring angle C—O—C to increase somewhat beyond the tetrahedral angle: in fact, in (5)–(9) the ring C—O—C angles lie in the range 113.0 (3)° for ring *A* in (7) to 114.9 (4)° for ring *D* of (6), with a mean value of *ca* 113.7°.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA5016). Services for accessing these data are described at the back of the journal.

Similar distortions of the chair conformation towards the boat form are also evident in (1), (3) and (4), although in (2) the uncertainties associated with the φ values preclude any analysis of the nature of the ring distortion in this compound.

3.2. Supramolecular structures

Where amino or hydroxyl groups are available, as in (8) and (9), the supramolecular aggregation is dominated by hard (Braga *et al.*, 1995; Desiraju & Steiner, 1999) hydrogen bonds of O—H···O, O—H···N and N—H···O types, and where these are present, the supramolecular structures are three dimensional. In derivatives where hard hydrogen bonds are not possible, soft hydrogen bonds of C—H···O type become dominant, giving a two-dimensional structure in (5) or three-dimensional structures as in (6) and (7). The structures of most of the compounds described here exhibit a substantial number
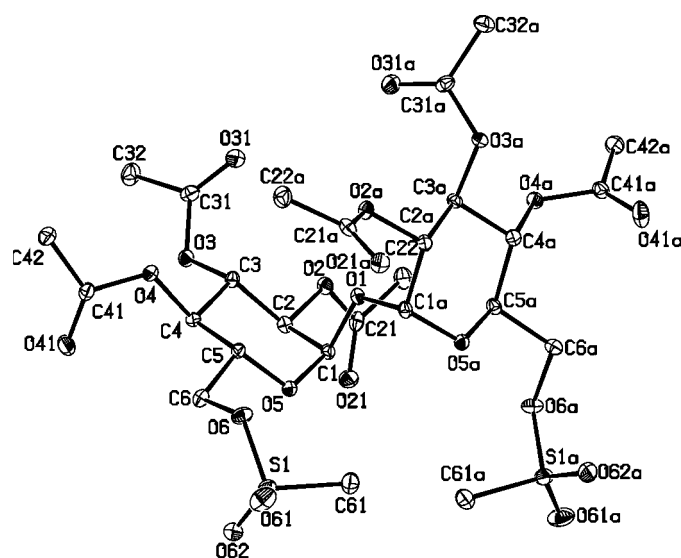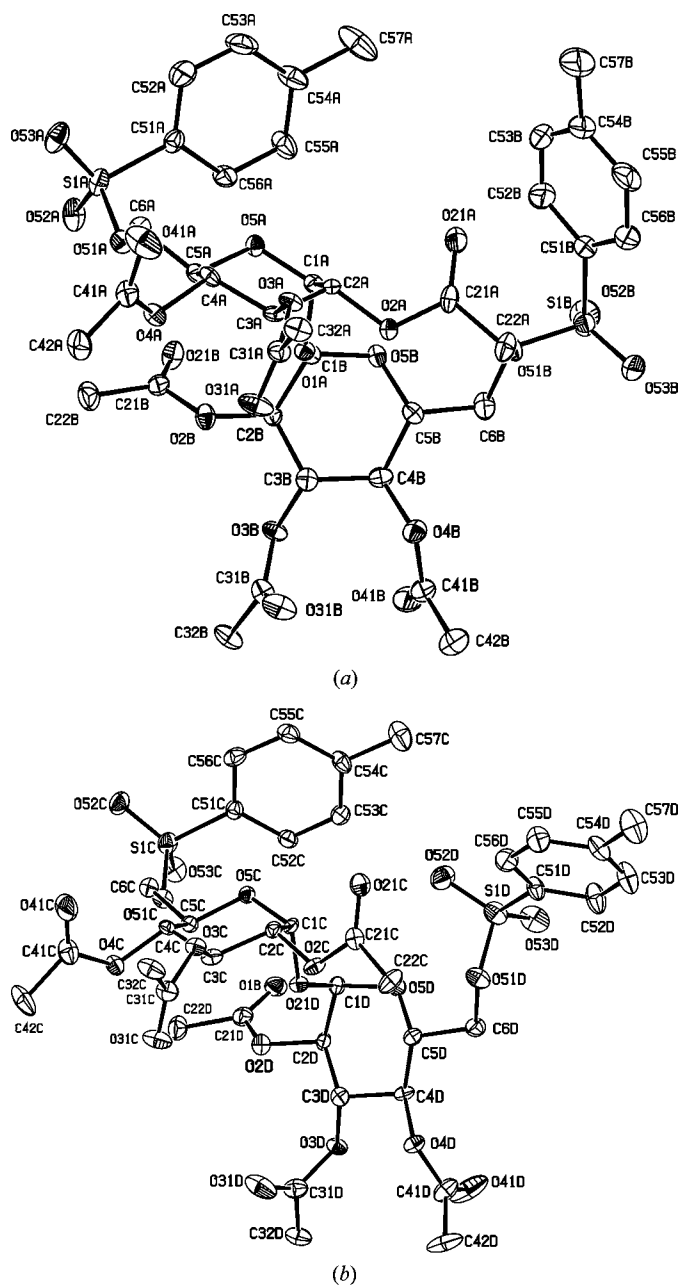

Figure 1
The molecule of (5) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(1 - x, y, 1 - z)$. For the sake of clarity the H atoms have been omitted.
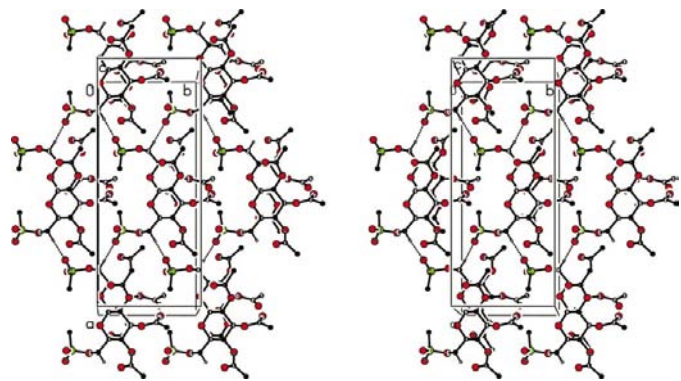
Figure 2
Stereoview of part of the crystal structure of (5) showing the formation of a (001) sheet of $R_4^4(36)$ rings. For the sake of clarity, the H atoms bonded to C atoms but not taking part in the motif shown are omitted.

of C—H···O contacts in which the H···O distances are close to the sum of their van der Waals radii. In general, we have considered only C—H···O interactions where the H···O distance is less than 2.55 Å and where the C—H···O angle exceeds 135°; however, contacts involving methyl groups have been discounted because of the rotational properties of these groups. Furthermore, because of the large numbers of contacts present, we have considered only the minimum numbers of the strongest interactions which suffice to define the dimensionality of the supramolecular structures.

3.2.1. Compound (5). Molecules of (5) (Fig. 1) lie across the rotation axes in the space group $C2$ and the reference mole-
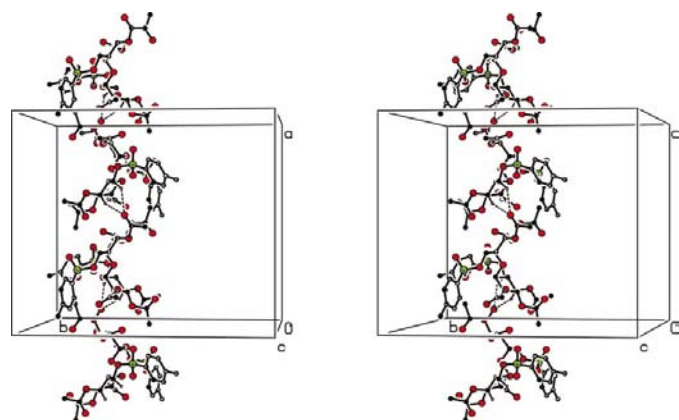

(a)

(b)

Figure 3
The two independent molecules of (6) showing the atom-labelling scheme: (a) molecule A; (b) molecule B. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity the H atoms have been omitted.

Table 3
Selected hydrogen-bond parameters (Å, °).

D—H···A	H···A	D···A	D—H···A
(5)			
C6—H6A···O61^{i}	2.43	3.221 (4)	136
(6)			
C4C—H4C···O41D^{ii}	2.46	3.365 (7)	150
C6C—H6F···O41D^{ii}	2.49	3.272 (6)	136
C55C—H55C···O31B^{iii}	2.41	3.313 (7)	160
C53D—H53D···Cg1^{iv}†	2.66	3.418 (7)	137
(7)			
C6A—H6B···O41B^{v}	2.32	3.268 (6)	160
C6B—H6C···O31A^{vi}	2.48	3.363 (8)	149
C6B—H6D···O41A^{vii}	2.52	3.400 (7)	148
(8)			
N1—H1A···O6W	2.05	2.835 (4)	165
O4—H4A···O61^{vi}	1.81	2.606 (3)	162
O6W—H6C···O31^{viii}	2.21	3.009 (4)	137
O6W—H6D···O4^{ix}	1.93	2.865 (3)	164
(9)			
O3—H3A···N1^{iii}	1.88	2.711 (3)	168
O4—H4B···O4^{x}	2.01	2.833 (3)	165
O6W—H6C···O3	1.74	2.667 (3)	155
O6W—H6D···O6W^{x}	1.75	2.733 (5)	165

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (ii) $-\frac{1}{2}+x, \frac{3}{2}-y, -z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (v) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (viii) $1-x, 1-y, -1+z$; (ix) $x, y, -1+z$; (x) $1-y, 1-x, \frac{1}{2}-z$. † Cg1 is the centroid of the ring C51C–C56C.

cule was selected as that across the axis along $(\frac{1}{2}, y, \frac{1}{2})$. A single C—H···O=S hydrogen bond (Table 3) links the molecules into sheets in which each molecule acts as a double donor and as a double acceptor of hydrogen bonds, such that each molecule is linked to four others. Atom C6 at (x, y, z), which is adjacent to the very electronegative sulfonyl unit, and which forms part of the molecule across the axis along $(\frac{1}{2}, y, \frac{1}{2})$, acts as a hydrogen-bond donor, via H6A, to sulfonyl O61 at $(\frac{1}{2}-x, \frac{1}{2}+y, 1-z)$, which forms part of the molecule whose central atom O1 is at $(0, \frac{1}{2}+y, \frac{1}{2})$. Similarly, O61 at (x, y, z) accepts a hydrogen bond from C6 at $(\frac{1}{2}-x, -\frac{1}{2}+y, 1-z)$, part of the

Figure 4
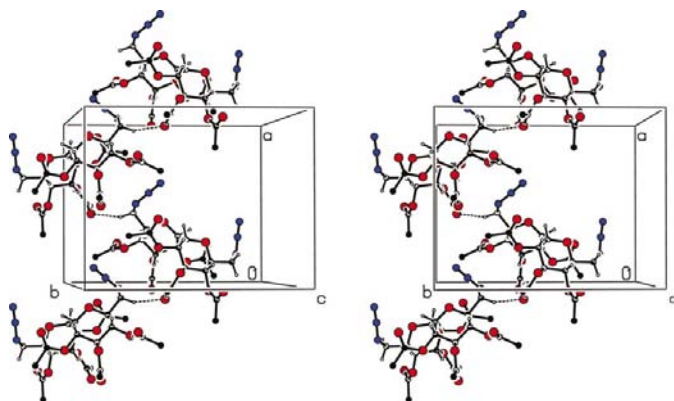Stereoview of part of the crystal structure of (6), showing the formation of a $C(13)C(13)[R_2^1(6)]$ chain of rings along [100]. For the sake of clarity, the H atoms bonded to C atoms but not taking part in the motif shown are omitted.
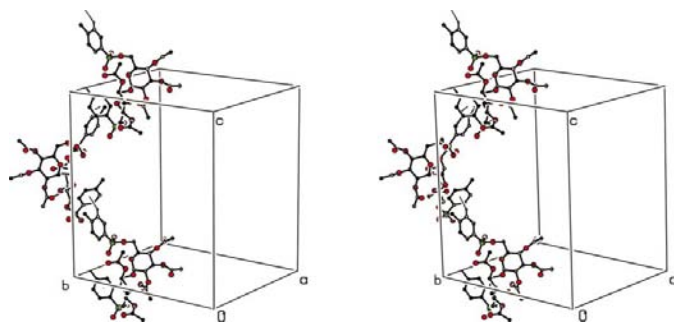
Figure 5
Stereoview of part of the crystal structure of (6) showing the formation of a chain along [001] generated by the C—H···π(arene) hydrogen bond. For the sake of clarity, the H atoms bonded to C atoms but not taking part in the motif shown are omitted.
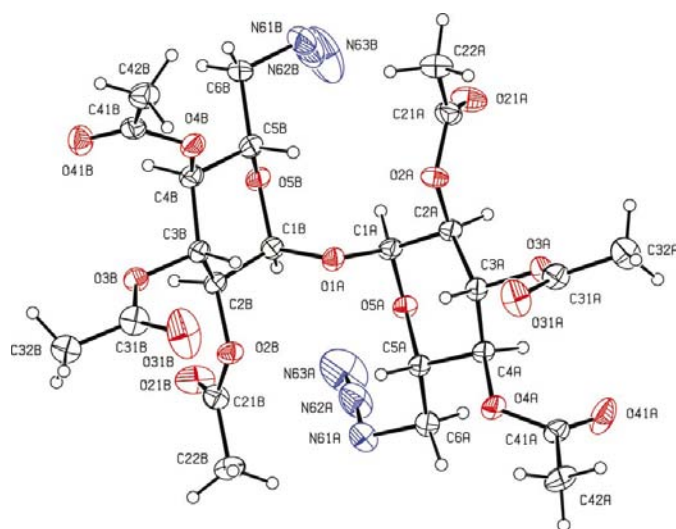
Figure 6
The trehalose molecule of (7) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, the partial ethanol solvate molecule is omitted.
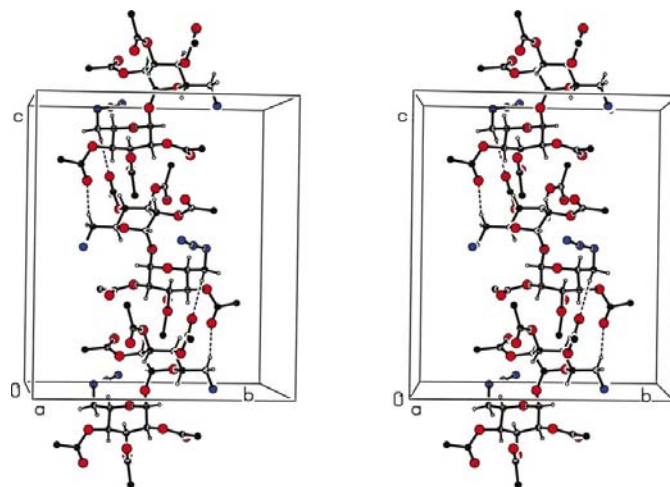

Figure 7
Stereoview of part of the crystal structure of (7) showing the formation of a $C(12)$ helical chain along [100]. For the sake of clarity the ethanol molecule is omitted and the H atoms bonded to C atoms but not taking part in the motif shown are omitted.

molecule whose O1 atom is at $(0, -\frac{1}{2} + y, \frac{1}{2})$. Propagation of this hydrogen bond by rotation then generates a deeply puckered (001) sheet in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(36)$ (Bernstein *et al.*, 1995) ring (Fig. 2).

There are no direction-specific interactions between adjacent sheets, but there is one rather short non-bonded contact, probably attractive, within the sheet. The atoms O31 at (x, y, z) and C61 at $(1 - x, 1 + y, 1 - z)$ are separated by only 2.973 (4) Å, rather less than the sum of the van der Waals radii, 3.22 Å (Bondi, 1964): since O31 is a carbonyl O, while methyl C61 is bonded to a sulfonyl group, these two atoms will be polarized as $O^{\delta-}$ and $C^{\delta+}$. Since the methyl group is almost certainly undergoing rapid rotation about the C—S bond, the associated C—H···O interaction is unlikely to be structurally significant.

3.2.2. Compound (6). Although (6) is very similar in chemical type to (5), both its crystallization behaviour and its supramolecular structure are rather different. Compound (6)

Figure 8
Stereoview of part of the crystal structure of (7) showing the formation of a chain of rings along [001]. For the sake of clarity the ethanol molecule is omitted and the H atoms bonded to C atoms but not taking part in the motif shown are omitted.
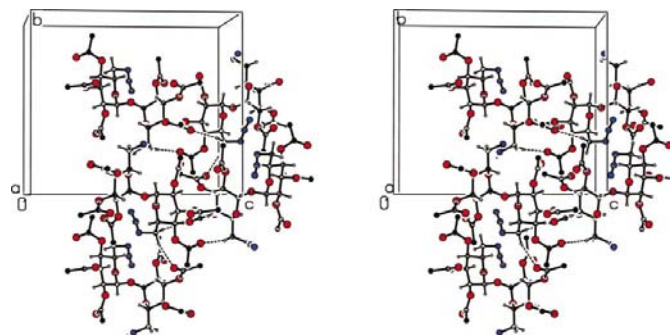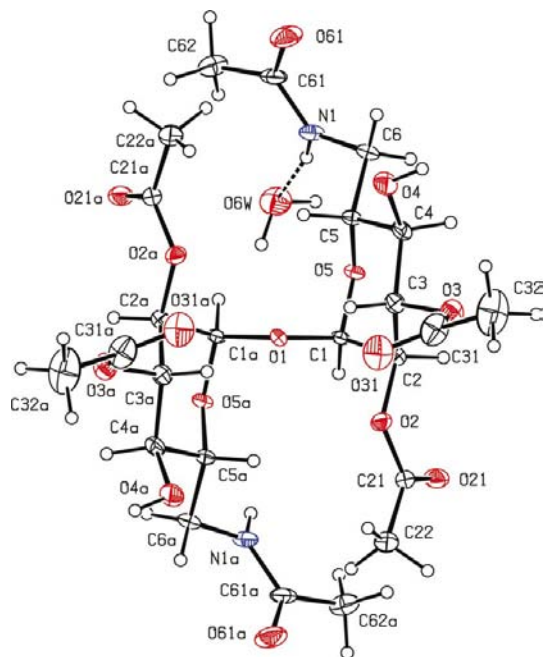

Figure 9
Stereoview of part of the crystal structure of (7) showing the formation of a chain along [010]. For the sake of clarity the ethanol molecule is omitted and the H atoms bonded to C atoms but not taking part in the motif shown are omitted.

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(Fig. 3) crystallizes with $Z' = 2$ in space group $P2_12_12_1$ [cf. $Z' = 0.5$ in C2 for (5)] and its supramolecular structure is based on a combination of three C—H$\cdots$O hydrogen bonds, with carbonyl O, rather than sulfonyl O, as the acceptor in each, together with a C—H$\cdots\pi$(arene) hydrogen bond (Table 3). On the other hand, aromatic $\pi\cdots\pi$ stacking interactions are absent from the structure of (6).

The molecules of type B, with O1B as the central atom, form a single three-dimensional framework from which the type A molecules, having O1A as the central atom, are pendent. The formation of the framework structure is most readily analysed in terms of the one-dimensional sub-structures (Gregson et al., 2000) generated by the C—H$\cdots$O and C—H$\cdots\pi$(arene) hydrogen bonds in turn.

In the type B molecule at (x, y, z), atoms C4C and C6C both act as hydrogen-bond donors, via H4C and H6F, respectively, to carbonyl atom O41D in the type B molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, -z)$, so producing a $C(13)C(13)[R_2^1(6)]$ chain of rings running parallel to the [100] direction and generated by the 2_1 screw axis along $(x, \frac{3}{4}, 0)$ (Fig. 4). A second, antiparallel chain of this type is generated by the 2_1 axis along $(-x, \frac{1}{4}, \frac{1}{2})$. The [100] chain is modestly reinforced by a dipolar interaction between nearly antiparallel carbonyl groups. The carbonyl group C21C—O21C in the type B molecule at (x, y, z) and the carbonyl group C21D—O21D in the type B molecule at $(-\frac{1}{2} + x, \frac{3}{2} - y, -z)$ lie in the same [100] chain of rings: the O21$C\cdots$C21D^i and C21$C\cdots$O21D^i distances [symmetry code: (i) $-\frac{1}{2} + x, \frac{3}{2} - y, -z$] are 2.958 (7) and 3.221 (7) Å, so forming a nearly rhomboidal type II (Allen et al., 1998) interaction.

The C—H$\cdots\pi$(arene) hydrogen bond also involves only the type B molecules and it gives rise to a chain parallel to [001]. The phenyl atom C53D in the type B molecule at (x, y, z) acts as a hydrogen-bond donor to the phenyl ring C51C—C56C in the type B molecule at $(\frac{1}{2} - x, 2 - y, \frac{1}{2} + z)$, giving a chain generated by the 2_1 screw axis along $(\frac{1}{4}, 1, z)$ (Fig. 5). The combination of the [100] and [001] chains, when propagated by the space group generates a continuous three-dimensional framework of type B molecules, to which the type A molecules are linked via a third C—H$\cdots$O hydrogen bond. The phenyl atom C55C in the type B molecule at (x, y, z) acts as a hydrogen-bond donor to the carbonyl O31B atom in the type A molecule at $(x, 1 + y, z)$: had the asymmetric unit been selected so that the two independent molecules were linked within it by this C—H$\cdots$O hydrogen bond, one of the molecules would necessarily have fallen entirely outside the unit cell.

3.2.3. Compound (7). Compound (7) crystallizes as a partial ethanol solvate in the space group $P2_12_12_1$ (Fig. 6): because of the low occupancy, 0.35, of the ethanol sites, only the interactions between disaccharide molecules will be discussed. The supramolecular aggregation is dominated by three C—H$\cdots$O hydrogen bonds (Table 3), all involving ring C—H bonds as donors and carbonyl O as acceptors; together they link the molecules into a continuous three-dimensional framework.

Atom C6B in the molecule at (x, y, z) acts as a hydrogen-bond donor, via H6C, to the carbonyl atom O31A in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, so forming a simple $C(12)$ chain running parallel to the [100] direction, and generated by the 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{2})$ (Fig. 7). A second chain of this type, antiparallel to the first, is generated by the 2_1 axis along $(-x, \frac{3}{4}, 0)$.

In a more complex motif, atoms C6A and C6B in the molecule at (x, y, z) act as hydrogen-bond donors, via H6B and H6D, respectively, to the carbonyl O atoms O41B in the
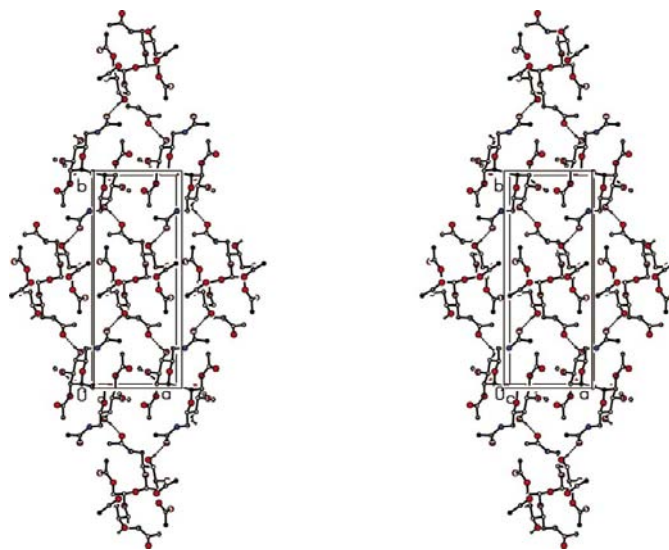

Figure 10
The molecule of (8), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(1 - x, 1 - y, z)$.

Figure 11
Stereoview of part of the crystal structure of (8) showing the formation of a (001) sheet of $R_4^4(44)$ rings. For the sake of clarity the water molecule is omitted, as are the H atoms bonded to C atoms.

molecule at $(\frac{3}{2} - x, 1 - y, -\frac{1}{2} + z)$ and O41A in the molecule at $(\frac{3}{2} - x, 1 - y, \frac{1}{2} + z)$ so forming a $C(13)C(13)[R_2^2(14)]$ chain of rings running parallel to the [001] direction and which is generated by the 2_1 screw axis along $(\frac{3}{4}, \frac{1}{2}, z)$ (Fig. 8). A second chain of this type, antiparallel to the first, is generated by the 2_1 axis along $(\frac{1}{4}, 0, -z)$.

The [100] and [001] chains are each generated by the repetition of just one of the interactions described above: the combination of the two interactions together generates a chain running parallel to the [010] direction (Fig. 9), and the combination of the [100], [010] and [001] chains generates the three-dimensional framework structure.

3.2.4. Compound (8). In (8) the substituted trehalose molecules lie across a twofold rotation axis in the space group $P2_12_12$, selected for the reference molecule as that along $(\frac{1}{2}, \frac{1}{2}, z)$, while the water molecule lies in a general position. In the selected asymmetric unit the water molecule is linked to the disaccharide by means of an N—H···O hydrogen bond (Table 3), so forming a compact three-molecule aggregate (Fig. 10). The supramolecular aggregation is then determined by the six hydroxyl or water O—H bonds available in each three-molecule aggregate for external hydrogen-bond formation. The construction of the resulting three-dimensional framework structure can then most readily be analysed in terms of the effect of each distinct hydrogen bond in turn.

The hydroxyl O4 atoms at (x, y, z) and $(1 - x, 1 - y, z)$ both lie in the reference disaccharide molecule whose central atom O1 lies at $(\frac{1}{2}, \frac{1}{2}, z)$. These two hydroxyl atoms act as hydrogen-bond donors, respectively, to atoms O61 at $(-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ and at $(\frac{3}{2} - x, \frac{1}{2} + y, 1 - z)$, which themselves lie in molecules whose central atoms are at $(0, 0, 1 - z)$ and $(1, 1, 1 - z)$, respectively. Similarly, the two atoms of type O61 in the reference molecule across $(\frac{1}{2}, \frac{1}{2}, z)$ accept hydrogen bonds from the O4 atoms at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, 1 - z)$, which lie, respectively, in molecules where the O1 atoms are at $(1, 0, 1 - z)$ and $(0, 1, 1 - z)$. In this manner, a single O—H···O hydrogen bond generates a (001) sheet in the form of a

(4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(44)$ ring (Fig. 11).

The (001) sheets are formed solely by the disaccharide components and they are linked into a three-dimensional framework by the water molecules. The water atom O6W at (x, y, z) acts as a hydrogen-bond donor, via H6D, to the hydroxyl atom O4 at $(x, y, -1 + z)$, so generating by translation a $C_2^2(8)$ chain parallel to the [001] direction, and the action of the twofold rotation axis converts this chain into a molecular ladder, in which parallel $C_2^2(8)$ chains act as the uprights and the disaccharide molecules as the rungs (Fig. 12). The combination of the [001] chains with the (001) sheets is sufficient to produce a three-dimensional structure, but this is further reinforced by a third O—H···O hydrogen bond. The water atom O6W at (x, y, z), which lies in the reference (001) sheet, acts as a hydrogen-bond donor via H6C to the acetato atom O31 at $(1 - x, 1 - y, -1 + z)$, which lies in the adjacent sheet along [001], again linking adjacent sheets.

3.2.5. Compound (9). The diaminotrehalose molecules in (9) lie across twofold rotation axes in the space group $P4_32_12$, selected for the reference molecule as that having $z = 0$, $x = y$;
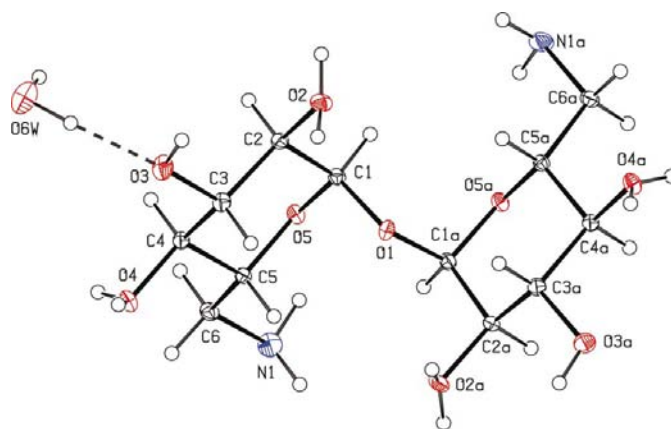
Figure 13
The independent molecular components of compound (9) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(y, x, -z)$.
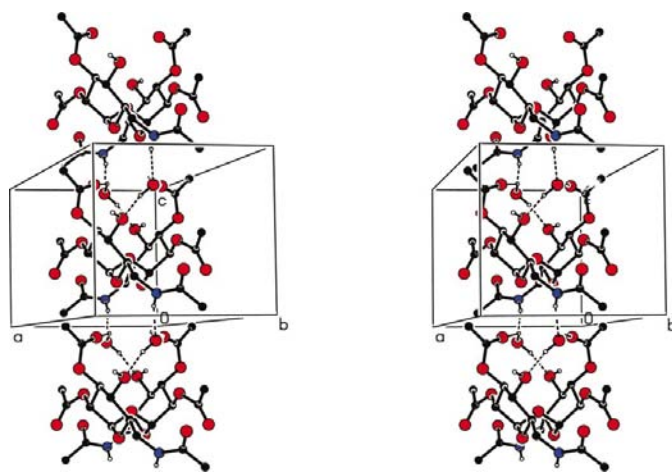
Figure 12
Stereoview of part of the crystal structure of (8) showing the formation of a molecular ladder along [001]. For the sake of clarity, the H atoms bonded to C atoms are omitted.
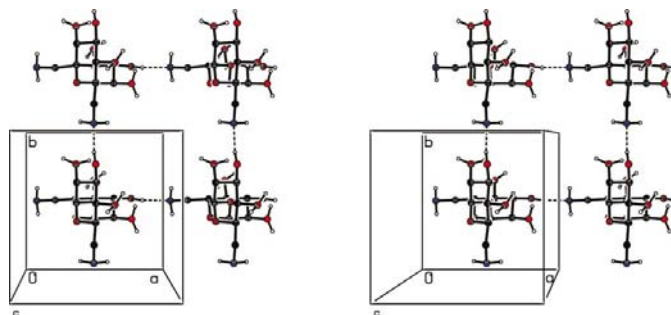
Figure 14
Stereoview of part of the crystal structure of (9) showing the formation of a (001) sheet of $R_4^4(44)$ rings. For the sake of clarity the water molecule is omitted, as are the H atoms bonded to C atoms.

there is also a water molecule lying in a general position and in the selected asymmetric unit (Fig. 13) this water molecule is linked to the disaccharide *via* an O—H···O hydrogen bond (Table 3). With no acyl substituents present, there is an extensive series of hydrogen bonds present in the structure, encompassing O—H···O, O—H···N and N—H···O types. However, the three-dimensional nature of the supramolecular structure can be readily established in terms of just two hydrogen bonds, in addition to that within the asymmetric unit; one of these hydrogen bonds generates sheets and the second links the sheets into a three-dimensional framework. The other hydrogen bonds can be regarded as reinforcing elaborations.

The hydroxyl atom O3 at (x, y, z) acts as a hydrogen-bond donor to the amino atom N1 at $(x, 1 + y, z)$, so generating by translation a $C(7)$ chain running parallel to the [010] direction: the action of the twofold axes through the molecules generates a similar chain running parallel to the [100] direction and the combination of these two chain motifs generates a (001) sheet in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(44)$ ring and involving only a single O—H···N hydrogen bond (Fig. 14). It may be noted here that although the gross topology of the (001) sheets in (8) and (9) is the same, the sheet in (8) is generated by a combination of twofold rotation and screw axes, whereas that in (9) is generated by a combination of translation and twofold rotation axes.

There are two interactions which link the (001) sheets into a continuous framework. Atom O4 at (x, y, z) lies in the (001) sheet whose twofold rotation axes are at $z = 0$; this atom acts as a hydrogen-bond donor, *via* H4*B*, to O4 at $(1 - y, 1 - x, \frac{1}{2} - z)$, which lies in the sheet with its axes at $z = \frac{1}{2}$. Although the occupancy of the H4*B* site is only 0.5, there is no necessary correlation between the occupancy of the H4*A* and H4*B* sites throughout a given sheet and hence 50% of the

H4*B* sites in any sheet will be available to form this hydrogen bond. In an entirely similar way, the water atom O6*W*, which is linked to the $z = 0$ sheet *via* O3 (Table 3), acts as a hydrogen-bond donor, *via* H6*D*, to O6*W* at $(1 - y, 1 - x, \frac{1}{2} - z)$, which is linked to the sheet at $z = \frac{1}{2}$. Propagation of these interactions by rotation and translation then links each (001) sheet to the two adjacent sheets, forming a chain of rings along the [001] direction (Fig. 15).

4. Concluding comments

It is striking how little the conformations of the pyranose rings in substituted α,α'-trehalose molecules are affected either by the extent of the substitution or by the steric bulk of the substituents: this is clearly illustrated at the extremes of the range of substitution considered here by (3) and (9) [see (I)], where the ring-puckering behaviour is essentially identical for the two compounds. On the other hand, the direction-specific intermolecular forces are very strongly influenced by the substitution pattern, with (4)–(9) forming a supramolecular structure (4) in one dimension, (5) in two dimensions and (6)–(9) three dimensions, while (1)–(3) contain effectively isolated molecules.

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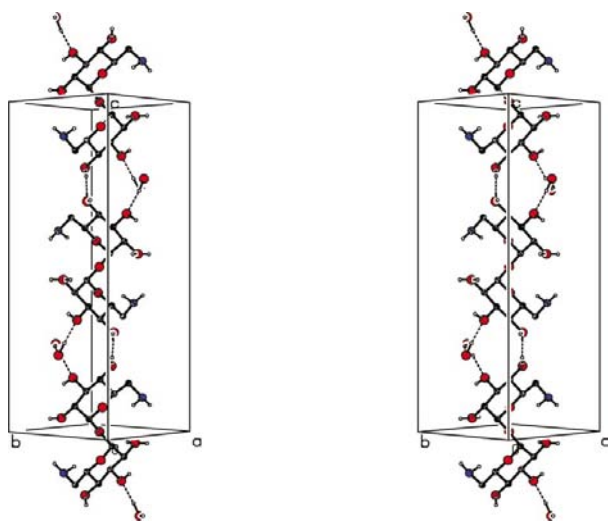
Figure 15
Stereoview of part of the crystal structure of (9) showing the formation of a chain of rings along [001], which links the (001) sheets. For the sake of clarity, the H atoms bonded to C atoms are omitted.

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