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Molecular and crystal structures of *N*-aryl-β-D-glycopyranosylamines from mannose and galactose

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Abstract

The molecular and crystal structures of 12 *N*-aryl-β-D-glycopyranosylamines have been determined by X-ray crystallography. Six of these are mannose derivatives, the *N*-*p*-bromophenyl (**1**), *N*-*p*-tolyl (**2**), *N*-*m*-chlorophenyl (**3**), *N*-*p*-methoxyphenyl (**4**), *N*-*o*-chlorophenyl (**5**), and *N*-*o*-tolyl (**6**) derivatives that are formed by reaction with the corresponding substituted anilines. The remaining six are galactose derivatives, the *N*-phenyl (**7**), *N*-*p*-chlorophenyl (**8**), *N*-*p*-bromophenyl (**9**), *N*-*p*-iodophenyl (**10**), *N*-*p*-nitrophenyl (**11**) and *N*-*p*-tolyl (**12**), derivatives prepared similarly. Compounds **1**–**3** assume the same packing arrangement. Compounds **4**, **5**, and **6** assume unique packing arrangements, although that assumed by **4** is closely related to that assumed by **1**–**3**. Compounds **7**–**11** assume the same packing arrangement; that assumed by **12** is closely related to that assumed by **7**–**11**. That the same packing arrangements can be maintained in spite of substantial changes in the electronic and steric nature of the substituent on the aryl ring reflects the strength of the hydrogen bond network connecting the monosaccharide portions of the molecules in the solid state. A hydrogen bonding motif found in all six mannose structures is a mutual interaction between translationally related molecules involving O-3–H···O-5 and O-6–H···O-4 hydrogen bonds. The recurrence of this motif throughout this group of mannosylamines suggests that it is an especially favorable interaction that might be expected to occur also in related macromolecular systems.

Keywords: X-ray crystal structure; Glycosylamines; Hydrogen bonding; Monosaccharides, structure; Mannose derivatives; Galactose derivatives

1. Introduction

Reaction of a monosaccharide with a nitrogenous base yields a derivative that could exist as an open-chain Schiff base or as a cyclic glycosylamine (Scheme 1). An understanding of the conditions that determine which linkage actually forms between a given base and given monosaccharide could lend insight into the nature of similar linkages important in macromolecular systems, such as the N-glycosylic linkage connecting carbohydrates to asparagine residues in glycoproteins[1,2] and the semicarbazide linkage connecting biotinylated labeling agents to oligosaccharides.[3–5] Previous studies in solution and in the solid state have shown that whether the monosaccharide derivative is a cyclic or acyclic compound depends on such

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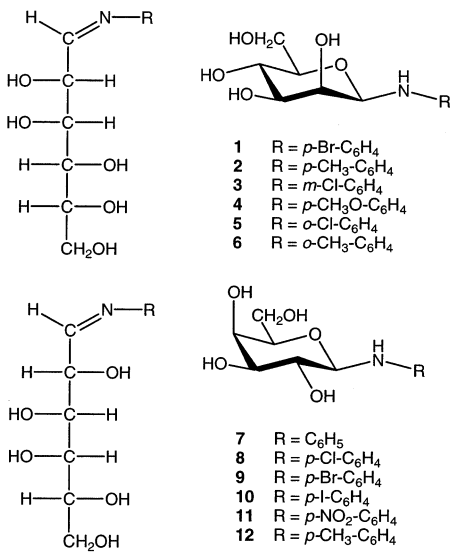
factors as the identity of the monosaccharide, the strength of the base, and the proton-accepting ability of the solvent.[6] Different monosaccharides yield different products, reaction of D-glucose with hydroxylamine yielding a crystalline *N*-glucopyranosylhydroxylamine but reaction of D-arabinose with hydroxylamine yielding crystalline syn and anti forms of the open-chain oxime.[7,8] Moreover, its behavior with hydroxylamine notwithstanding, D-arabinose reacts with *p*-bromophenylhydrazine to form a crystalline arabinopyranosylamine[9] as does L-arabinose upon reaction with *p*-toluenesulfonylhydrazide.[10] In each case it is likely that an equilibrium between the various forms is in effect in solution, but which form ultimately will crystallize from solution is not readily predicted, the form predominant in the solid state not necessarily being the form predominant in solution.[6,11]

Both Schiff bases and glycosylamines might result also from the reaction of monosaccharides with primary aromatic amines. In the early literature concerning the question of whether sugar 'anilides' assume cyclic or acyclic structures, opinion on this point was divided,[12–15] but spectroscopic and X-ray crystallographic evidence supporting the cyclic form has accumulated since.[16–19] Recently, by means of X-ray crystallography, we determined the molecular and crystal structures of two cyclic derivatives of this type, *N*-phenylmannopyranosylamine and *N*-(*p*-chlorophenyl)mannopyranosylamine, as well as the structures of the open-chain oxime and the cyclic semicarbazide derivative of D-mannose.[20] We found the preference of the mannose 'anilide' for the cyclic form to be particularly interesting, given that mannose phenylhydrazone, which differs from the 'anilide' in composition by only a single –NH-group, is an open-chain compound in the solid state.[21] These results raised the question of whether the reaction of a monosaccharide with a primary aromatic amine would always yield a crystalline glycosylamine regardless of the nature (such as electron-donating versus electron-withdrawing) of any substituents present on the aromatic ring. Beyond the question of the cyclic or acyclic nature of the derivative, we also wished to address the larger question of whether a study of these small-molecule systems would reveal characteristic structural features (such as preferred hydrogen-bonding patterns) that could also apply to macromolecular systems. We subsequently prepared a series of these derivatives differing in their ring substitution and determined their structures by means of X-ray crystallography. In each case the derivative was found to be a glycopyranosylamine. In this report we describe the molecular and crystal structures of six mannopyranosylamines, the *N*-*p*-bromophenyl (**1**), *N*-*p*-tolyl (**2**), *N*-*m*-chlorophenyl (**3**), *N*-*p*-methoxyphenyl (**4**), *N*-*o*-chlorophenyl (**5**), and *N*-*o*-tolyl (**6**) derivatives formed upon reaction of D-mannose with the corresponding substituted anilines. We also report here the molecular and crystal structures of six galactopyranosylamines, the *N*-phenyl (**7**), *N*-*p*-chlorophenyl (**8**), *N*-*p*-bromophenyl (**9**), *N*-*p*-iodophenyl (**10**), *N*-*p*-nitrophenyl (**11**), and *N*-*p*-tolyl (**12**) derivatives formed upon reaction of D-galactose with the corresponding anilines.



Scheme 1. Schiff base (left) and β-D-glycosylamine (right) forms of a derivative formed by reaction between D-mannose (top) or D-galactose (bottom) and a nitrogenous base R-NH_2. Compounds **1**–**12** occur as β-D-glycosylamines in the solid state.

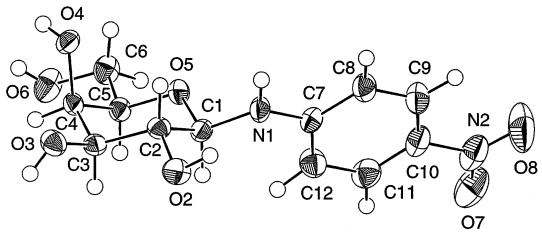


Fig. 1. ORTEPII[22] drawing of **11**, showing atom numbering. The ellipsoids are drawn at the 50% probability level.

2. Results and discussion

Molecular geometry.—An ORTEPII[22] view of **11** showing the atom numbering scheme and molecular conformation is given in Fig. 1. (Compound **11** was chosen for this view so that the orientation of the nitro group with respect to the phenyl ring could be shown.) Similar atom numbering schemes apply to **1**–**10** and **12**. All of these compounds are cyclic in the solid state, occurring as β-D-mannopyranosylamines or β-D-galactopyranosylamines having the $^4C_1$ conformation. Cremer–Pople puckering parameters[23–25] (calculated using the program PLATON-94[26]) and asymmetry parameters ΔC_s[27] (also from PLATON-94) for compounds **1**–**12** are given in Table 1. In most of these structures the effects on bond lengths of changing the nature or position of the aryl substituent are minimal, bonds such as O-5–C-1, N-1–C-1, and N-1–C-7 showing no significant differences in length from structure to structure. An exception is the nitro-substituted compound **11**, which has an N-1–C-7 bond length of 1.381(3) Å as opposed to lengths of 1.401–1.410 Å for this bond found in the other galactopyranosylamines examined here. Lengths for this bond of 1.377(5) Å and 1.383(3) Å have been reported for *N*-*p*-nitrophenyl-*N*-(2,3,4-tri-*O*-acetyl-β-D-lyxopyranosyl)amine and *N*-*p*-nitrophenyl - *N* - (2,3,4 - tri - *O* - acetyl - α - L-

Table 1
Cremer–Pople puckering parameters and asymmetry parameters

	1	**2**	**3**
Q (Å)	0.567(5)	0.563(2)	0.559(3)
Θ (°)	5.7(4)	4.9(2)	2.5(3)
Φ (°)	348.8(49)	1.3(32)	358.1(68)
ΔC_S(C-1, C-4) (°)	9.5(4)	7.36(17)	6.2(2)
ΔC_S(C-2, C-5) (°)	7.5(4)	7.39(19)	5.7(2)
ΔC_S(C-3, O-5) (°)	2.1(4)	0.3(2)	0.8(2)
	4 [a]	**5**	**6**
Q (Å)	0.565(12); 0.574(12)	0.602(4)	0.594(2)
Θ (°)	3.8(11); 175.9(11)	4.4(4)	2.8(2)
Φ (°)	360.0(180); 170.4(170)	25.3(53)	22.6(37)
ΔC_S(C-1, C-4) (°)	7.2(9); 6.9(10)	6.2(3)	5.45(16)
ΔC_S(C-2, C-5) (°)	7.3(10); 6.8(10)	7.8(3)	6.55(16)
ΔC_S(C-3, O-5) (°)	0.8(10); 0.9(10)	1.7(3)	1.15(16)
	7	**8**	**9**
Q (Å)	0.591(2)	0.586(2)	0.570(4)
Θ (°)	3.3(3)	3.6(3)	2.3(4)
Φ (°)	300.1(42)	273.4(38)	272.2(65)
ΔC_S(C-1, C-4) (°)	6.48(19)	5.53(16)	5.4(3)
ΔC_S(C-2, C-5) (°)	3.57(19)	2.07(16)	1.9(3)
ΔC_S(C-3, O-5) (°)	3.30(17)	4.09(16)	4.5(3)
	10	**11**	**12** [a]
Q (Å)	0.648(49)	0.589(2)	0.584(3); 0.592(3)
Θ (°)	5.6(45)	2.8(3)	4.1(3); 3.6(3)
Φ (°)	295.3(459)	263.4(61)	248.2(53); 253.1(36)
ΔC_S(C-1, C-4) (°)	9(4)	4.90(16)	3.8(2); 4.2(2)
ΔC_S(C-2, C-5) (°)	4(4)	2.57(16)	1.7(2); 1.6(2)
ΔC_S(C-3, O-5) (°)	8(4)	2.66(16)	3.6(2); 4.8(2)

[a] First entry refers to O-5 ring; second entry refers to O-25 ring.

Table 2
Selected torsional angles (°)

	1	2	3
O-5–C-1–N-1–C-7	−76.1(5)	−69.9(2)	−74.6(3)
O-5–C-5–C-6–O-6	74.9(5)	74.0(2)	73.6(3)
O-6–C-6–C-5–C-4	−164.5(4)	−164.7(2)	−164.9(2)
C-1–N-1–C-7–C-8	−175.7(4)	179.2(2)	172.1(3)
C-1–N-1–C-7–C-12	1.7(7)	−2.4(3)	−9.2(5)
C-2–C-1–N-1–C-7	164.0(4)	169.2(2)	165.2(3)
	4 [a]	**5**	**6**
O-5–C-1–N-1–C-7	−69.9(3); −70.0(3)	−67.4(3)	−67.0(3)
O-5–C-5–C-6–O-6	73.1(3); 73.7(3)	47.6(3)	−64.9(2)
O-6–C-6–C-5–C-4	−165.1(2); −164.6(2)	166.7(2)	57.4(2)
C-1–N-1–C-7–C-8	−177.6(3); 176.7(2)	−178.1(3)	179.6(2)
C-1–N-1–C-7–C-12	2.2(4); −6.7(4)	2.2(5)	−0.9(3)
C-2–C-1–N-1–C-7	169.1(2); 169.0(2)	173.0(3)	171.1(2)
C-9–C-10–O-7–C-13	−167.4(4); −7.1(5)		
C-11–C-10–O-7–C-13	8.4(5); 175.0(3)		
	7	**8**	**9**
O-5–C-1–N-1–C-7	−70.7(3)	−73.9(2)	−74.8(4)
O-5–C-5–C-6–O-6	175.2(2)	−179.8(2)	179.8(2)
O-6–C-6–C-5–C-4	−62.3(3)	−57.4(3)	−55.8(4)
C-1–N-1–C-7–C-8	167.6(2)	170.1(2)	171.0(3)
C-1–N-1–C-7–C-12	−16.1(4)	−13.5(4)	−11.4(6)
C-2–C-1–N-1–C-7	167.6(2)	165.1(2)	164.0(3)
	10	**11**	**12**[a]
O-5–C-1–N-1–C-7	−76.9(10)	−76.2(3)	−73.5(3); −75.6(3)
O-5–C-5–C-6–O-6	179.7(6)	178.4(2)	179.2(2); −179.9(2)
O-6–C-6–C-5–C-4	−58(1)	−60.1(3)	−58.1(3); −58.0(3)
C-1–N-1–C-7–C-8	172.9(9)	167.9(2)	158.1(2); −176.0(2)
C-1–N-1–C-7–C-12	−10(1)	−13.6(4)	−25.2(4); 2.5(4)
C-2–C-1–N-1–C-7	163.7(7)	163.2(2)	165.8(2); 163.0(2)
C-9–C-10–N-2–O-7		−173.1(3)	
C-9–C-10–N-2–O-8		6.7(4)	
C-11–C-10–N-2–O-7		6.0(4)	
C-11–C-10–N-2–O-8		−174.2(3)	

[a] Two independent molecules in the asymmetric unit. For the names of the atoms defining the second torsional angle, add 20 to the atom number of each atom defining the first torsional angle.

arabinopyranosyl)amine, respectively, in which delocalization of the electron pair from the glycosidic nitrogen into the nitro-substituted aryl ring has been suggested.[17]

Selected torsional angles for **1**–**12** are listed in Table 2. The torsional angles defining the aglycone conformation do not vary greatly from structure to structure in spite of the differences in aryl ring substitution. In all cases, the *gauche* O-5–C-1–N-1–C-7 torsional angle places the N-1–C-7 bond in a staggered orientation with respect to the C-1–H-1 and C-1–O-5 bonds and anti with respect to the C-1–C-2 bond. This corresponds to the *E*1 conformation reported to be especially stable for pyranosides.[28] The orientation of the substituent in the structures of the meta-substituted compound **3** and the ortho-substituted compounds **5** and **6** is outward and away from the monosaccharide. Of all the mannopyranosylamines we have examined thus far, only one, compound **6**, does not have the *gt* conformation at the C-6–O-6 side chain. In **6** this conformation is *gg*. In all of the galactopyranosylamine structures included here, the conformation of the C-6–O-6 side chain is *tg*.[29] In **4** the two molecules in the asymmetric unit are distinguished from each other by the different orientations of their methoxy substituents; in **12** the two are distinguished by a difference in

Table 3
Hydrogen-bond parameters[a]

	D–H···A	D···A (Å)	D–H···A (°)
1	O-2–H-20···O-4^{i}	3.037(6)	149
	O-3–H-30···O-5^{ii}	2.815(4)	156
	O-4–H-40···O-3^{iii}	2.735(4)	141
	O-6–H-60···O-4^{iv}	2.792(4)	141
	N-1–H-70···O-6^{i}	3.114(6)	150
2	O-2–H-20···O-4^{i}	2.943(2)	155(3)
	O-3–H-30···O-5^{ii}	2.798(2)	171(2)
	O-4–H-40···O-3^{iii}	2.704(2)	175(3)
	O-6–H-60···O-4^{iv}	2.772(2)	171(2)
	N-1–H-70···O-6^{i}	3.113(3)	156(2)
3	O-2–H-20···O-4^{i}	2.995(3)	150(4)
	O-3–H-30···O-5^{ii}	2.793(3)	178(4)
	O-4–H-40···O-3^{iii}	2.727(3)	172(4)
	O-6–H-60···O-4^{iv}	2.758(3)	172(4)
	N-1–H-70···O-6^{i}	3.133(4)	148(3)
4	O-2–H-20···O-4^{i}	2.927(3)	151(3)
	O-3–H-30···O-25^{ii}	2.809(2)	170(3)
	O-4–H-40···O-23^{v}	2.706(3)	165(3)
	O-6–H-60···O-24^{vi}	2.792(3)	161(3)
	N-1–H-70···O-6^{i}	3.134(3)	162(3)
	O-22–H-220···O-24^{i}	2.927(3)	149(3)
	O-23–H-230···O-5^{vi}	2.805(2)	172(3)
	O-24–H-240···O-3^{v}	2.709(3)	177(3)
	O26–H-260···O-4^{iv}	2.763(3)	176(3)
	N-21–H-270···O-26^{i}	3.098(3)	151(2)
5	O-2–H-20···O-6^{vii}	2.673(3)	146
	O-3–H-30···O-2^{i}	3.136(3)	144(3)
	O-3–H-30···O-5^{i}	3.127(3)	145(3)
	O-4–H-40···O-3^{viii}	2.781(3)	158
	O-6–H-60···O-4^{ix}	2.718(3)	163(4)
6	O-2–H-20···O-3^{x}	2.727(2)	169(3)
	O-3–H-30···O-5^{xi}	2.850(2)	169(2)
	O-4–H-40···O-6^{xii}	2.666(2)	165(3)
	O-6–H-60···O-4^{xiii}	2.653(2)	156(3)
7	O-2–H-20···O-6^{ix}	2.793(3)	151(3)
	O-3–H-30···O-4^{iv}	2.882(3)	161(3)
	O-4–H-40···O-2^{xiv}	3.201(3)	127(3)
	O-4–H-40···O-3^{xiv}	2.964(3)	163(3)
	O-6–H-60···O-3^{xiv}	2.819(3)	149(3)
	O-6–H-60···O-4^{xiv}	3.212(3)	136(3)
	N-1–H-70···O-2^{ii}	3.198(3)	171(3)
8	O-2–H-20···O-6^{ix}	2.722(2)	161(3)
	O-3–H-30···O-4^{iv}	2.808(2)	155(3)
	O-4–H-40···O-2^{xiv}	3.106(2)	130(3)
	O-4–H-40···O-3^{xiv}	2.936(2)	158(3)
	O-6–H-60···O-3^{xiv}	2.796(2)	161(3)
	O-6–H-60···O-4^{xiv}	3.258(2)	122(2)
	N-1–H-70···O-2^{ii}	3.107(3)	168(3)
9	O-2–H-20···O-6^{ix}	2.715(4)	158
	O-3–H-30···O-4^{iv}	2.806(3)	137
	O-4–H-40···O-2^{xiv}	3.090(3)	104
	O-4–H-40···O-3^{xiv}	2.950(3)	159
	O-6–H-60···O-3^{xiv}	2.784(4)	161
	O-6–H-60···O-4^{xiv}	3.247(4)	117
	N-1–H-70···O-2^{ii}	3.100(4)	156
10	O-2–H-20···O-4^{iii}	3.080(9)	90(10)
	O-2–H-20···O-6^{ix}	2.741(9)	161(15)
	O-3–H-30···O-4^{iii}	2.946(8)	138
	O-4–H-40···O-3^{ii}	2.830(9)	121
	O-6–H-60···O-3^{xiv}	2.783(9)	144(13)
	O-6–H-60···O-4^{xiv}	3.273(9)	117(11)
	N-1–H-70···O-2^{ii}	3.11(1)	168
11	O-2–H-20···O-6^{ix}	2.707(3)	152(2)
	O-3–H-30···O-4^{iv}	2.810(3)	164(3)
	O-4–H-40···O-2^{xiv}	3.226(2)	129(3)
	O-4–H-40···O-3^{xiv}	2.930(2)	160(3)
	O-6–H-60···O-3^{xiv}	2.802(2)	147(3)
	O-6–H-60···O-4^{xiv}	3.241(3)	139(3)
	N-1–H-70···O-2^{ii}	3.098(3)	160(3)
12	O-2–H-20···O-6^{ix}	2.733(2)	152(3)
	O-3–H-30···O-24^{vi}	2.790(3)	164(3)
	O-4–H-40···O-22^{xv}	3.079(2)	113(2)
	O-4–H-40···O-23^{xv}	2.966(2)	170(3)
	O-6–H-60···O-23^{xv}	2.778(3)	158(3)
	O-22–H-220···O-26^{ix}	2.723(3)	156(3)
	O-23–H-230···O-4^{iv}	2.806(2)	157(3)
	O-24–H-240···O-2^{xv}	3.042(3)	135(3)
	O-24–H-240···O-3^{xv}	2.948(2)	151(3)
	O-26–H-260···O-3^{xv}	2.763(3)	161(3)
	O-26–H-260···O-4^{xv}	3.273(3)	122(2)
	N-1–H-70···O-22^{ii}	3.132(3)	174(3)
	N-21–H-270···O-2^{vi}	3.104(3)	164(3)

[a] Symmetry codes: (i) $x, 1+y, z$; (ii) $-1+x, y, z$; (iii) $1-x, -1/2+y, 1-z$; (iv) $1+x, y, z$; (v) $-x, -1/2+y, -z$ (vi) xyz; (vii) $-1/2+x, 1/2+y, z$; (viii) $-x, y, -z$; (ix) $x, -1+y, z$; (x) $1/2-x, 1-y, -1/2+z$; (xi) $x, y, 1+z$; (xii) $-1/2-x, 1-y, 1/2+z$; (xiii) $x, y, -1+z$; (xiv) $1-x, 1/2+y, 1-z$; (xv) $-x, 1/2+y, -1-z$.

the twist of the aryl ring with respect to the monosaccharide.

Packing arrangements and intermolecular interactions.—An unanticipated result of these structure determinations was finding that even a substantial change in the ring substituent not only had no effect on the structure of the derivative (at least in determining whether it was cyclic or acyclic) but also in many cases had no effect on its packing arrangement. Among these mannopyranosylamines, compounds **1**–**3** are isostructural with each other and with the previously reported *N*-(*p*-chlorophenyl)mannopyranosylamine. Among

these six galactopyranosylamines, only two packing arrangements are represented, and only compound **12** assumes a unique one. Moreover, the packing arrangement assumed by **12** is closely related to that assumed by **7**–**11**. This isostructuralism occurs in spite of differences in ring substitution that include not only simple halogen-for-halogen exchanges but also replacement of the halogens with a hydrogen atom, the methyl group, and the nitro group, substituents that are significantly different from the halogens sterically and electronically. In **3**, even the replacement of a para substituent with a meta substituent leaves the packing arrangement undisturbed. On the other hand, we have also found that certain of these derivatives that might be expected to assume similar packing arrangements because of the similarity of their ring substituents actually do not. The ortho-substituted mannopyranosylamines **5** and **6**, related by the exchange of a chlorine atom for a methyl group, assume unique packing arrangements even though the para-substituted analogues are isostructural with each other.

Details of the hydrogen bonding in **1**–**12** are given in Table 3. In the mannopyranosylamine series, each of the potential hydrogen bond donor atoms does in fact serve as a donor in at least one of these structures, although approaches involving the N–H bond are not very close. With the exception of a weak interaction in **5**, O-2 does not serve as an acceptor atom in any of the structures **1**–**6**, nor does N-1, but the remaining potential acceptors O-3, O-4, O-5, and O-6 all do. In the galactopyranosylamine series, only O-5 does not serve as an acceptor. All of the potential donors participate in hydrogen bonding, but again the N–H interactions are not especially close. The nitro group of **11** does not participate in hydrogen bonding, unlike the nitro group of a similar galactopyranoside reported recently, 2-nitrophenyl 1-thio-β-D-galactopyranoside.[30]

The packing arrangement assumed by **1** is shown in Fig. 2; compounds **2**, **3**, and the *N*-(*p*-chlorophenyl)mannopyranosylamine described previously[20] pack in this same manner. Molecules in this packing arrangement are linked into chains extending along the *a* axis by two hydrogen-bonding interactions, O-3–H···O-5 $(-1+x,\ y,\ z)$ and O6–H···O-4 $(1+x,\ y,\ z)$, which define a ten-membered hydrogen-bonded ring connecting pairs of translationally related monosaccharides. The chains are connected side-by-side along the *b* axis, forming layers, by a pair of hydrogen bonds, O-2–H···O-4 $(x,\ 1+y,\ z)$ and N-1–H···O-6 $(x,\ 1+y,\ z)$, again linking translationally related molecules. Layers are stacked on top of each other along the *c* axis such that the monosaccharide moieties of a given layer interact with the monosaccharide moieties of a neighboring layer (an interaction involving a hydrogen bond, O-4–H···O-3 $(1-x,\ -1/2+y,\ 1-z)$) while the aryl rings of the given layer interact with the aryl rings of its other neighboring layer. This arrangement produces an alternating pattern of layers in the *c* direction that generates the screw axial symmetry of the packing and defines an alternating pattern of hydrophilic (monosaccharides) and hydrophobic (aryl groups) regions in the crystal. In *N*-phenylmannopyranosylamine[20] the stacking of layers is different, but the intermolecular hydrogen bonding pattern is the same as that found in **1**–**3** and in the *N*-(*p*-chlorophenyl)mannopyranosylamine structure.

In the early stages of the structure determination, the unit cell of **4** was found to be similar to those of **1**–**3** with the exception that

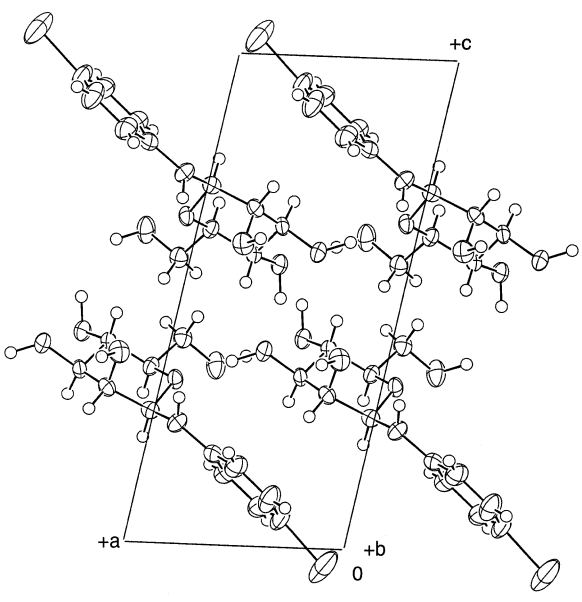


Fig. 2. Molecular packing in **1**.

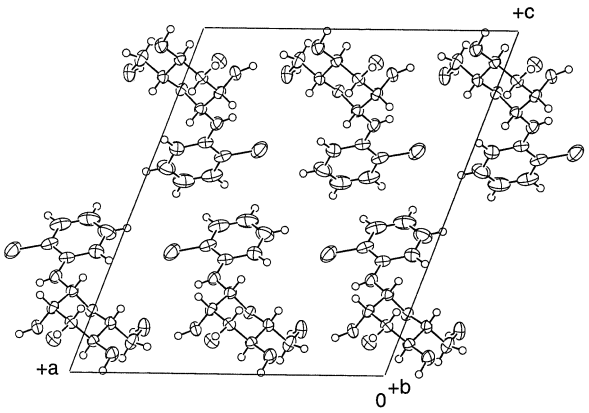


Fig. 3. Molecular packing in **5**.

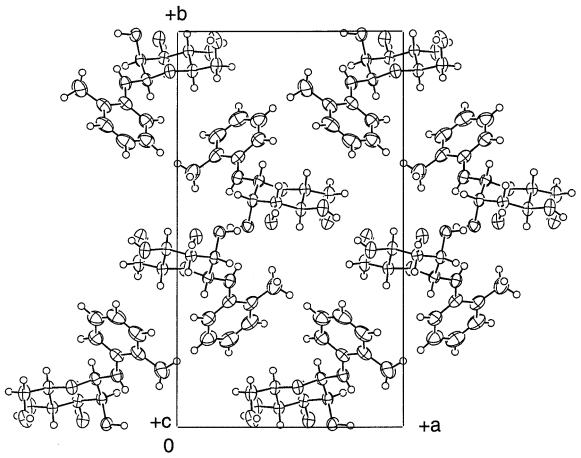


Fig. 4. Molecular packing in **6**.

the *a*-axis of **4** was approximately twice as long as the *a*-axes of the other compounds. The data support a structure in which the asymmetric unit of **4** contains two crystallographically independent molecules that differ primarily in the orientations of their methoxyl groups, as opposed to a cell half the size with a disordered methoxy group. The two different orientations may be the result of packing considerations, the different twists about the methoxyl C–O bond perhaps allowing the most efficient packing of (or minimizing collisions between) methoxyl groups (see Table 2 for relevant torsional angles). As it is, the approaches between neighboring methoxyl groups are close: O-7···C-13 $(1-x,\ 1/2+y,\ 1-z) = 3.146(5)$ Å; O-27···C-33 $(2-x,\ -1/2+y,\ 1-z) = 3.072(4)$ Å. Had these methoxyl group orientations been identical, only minor additional conformational adjustments would be required to make the two independent molecules identical and translationally related, the repeat distance along *a* would become half what was found, and the unit cell and the overall packing arrangement would become identical to those of **1**–**3**. In fact, the hydrogen bonding scheme found in **4** is essentially the same as that found in these other structures. The only significant difference is that certain hydrogen bonds linking molecules that are translationally related in **1**–**3** link molecules that are crystallographically independent in **4**.

The packing arrangement assumed by **5** is shown in Fig. 3. The isostructuralism between the *N*-(*p*-chlorophenyl)mannopyranosylamine and the *m*-chloro isomer **3** shows that the crystalline environment of C-9 in this packing arrangement is sufficiently uncrowded to allow the replacement of a hydrogen atom with a chlorine atom without disrupting the molecular packing. The fact that the *o*-chloro isomer **5** assumes a unique packing arrangement would suggest that the same cannot be said for the environment of C-8 in the structure assumed by **1**–**3**; however, it is possible that a polymorph of **5** isostructural with **1**–**3** could exist and simply has not yet been obtained under the crystallization conditions used here. Although the overall packing arrangement of **5** is different from that of **1**–**3**, a pair of intermolecular contacts found in **1**–**3** and also in **4**, the O-3–H···O-5 and O-6–H···O-4 hydrogen bonds linking translationally related molecules, are also found in **5**. The hydrogen bonding pattern of **5** includes a three-center hydrogen bond (sum of the angles O-3–H···O-2, O-3–H···O-5, and O-2···H···O-5 $\approx 360°$; 1.4 Å $<$ H···O-2 and H···O-5 $<$ 2.85 Å[31]).

Molecular packing in the *o*-methyl derivative **6** is shown in Fig. 4. As noted previously, methyl groups can serve as isosteric replacements for chlorine atoms and leave packing arrangements unaffected; however, the packing arrangement of **6** is unique, different even from that of the *o*-chloro compound **5**. In spite of the difference in packing, the O-3–H···O-5 and O-6–H···O-4 hydrogen bonds found in all the other mannopyranosylamines are also found in **6**. This is the only structure among the mannosylamines we have examined thus far in which the C-6–O-6 side chain

assumes a conformation other than *gt*. This fact may be further evidence that the pair of translational contacts O-3–H···O-5 and O-6–H···O-4 are important modes of intermolecular interaction for mannopyranosylamines. In the packing arrangement assumed by **6**, the translational O-6–H···O-4 contact is maintained if the C-6–O-6 side chain assumes the *gg* rather than the *gt* conformation. This conformation places O-6 in a position to serve as an acceptor in another hydrogen bond as well: O-4–H···O-6 $(-1/2-x,\ 1-y,\ 1/2+z) =$ 2.666(2) Å.

Compounds **7**–**11** assume the packing arrangement shown for **11** in Fig. 5. The molecules are linked pairwise at multiple points by hydrogen bonds between molecules related by screw-axial symmetry. The O-4 hydroxyl of a given molecule is positioned so that it can serve as an H-bond donor to either O-2 or O-3 of a neighboring screw-axially related molecule or to both of these potential acceptors. Similarly, O-6 of this same given molecule is positioned so that it can serve as an H-bond donor to either O-3 or O-4 or to both of these acceptors in the same neighboring screw-axially related molecule. Both the O-4 and O-6 interactions are potential three-center hydrogen bonds, judging from the hydrogen···acceptor distances (generally shorter than 2.85 Å) and the angles (sum of D–H···acceptor (1), D–H···acceptor (2), and acceptor (1)···H···acceptor (2) angles ≈ 360°). On the other hand, alternative interpretations of the hydrogen bond patterns are possible; a different donor–acceptor pattern is shown by

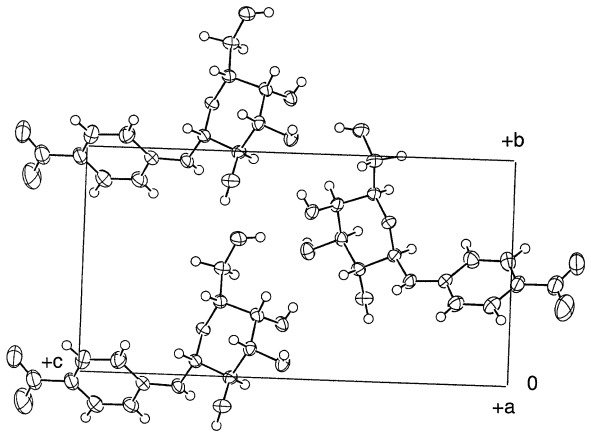


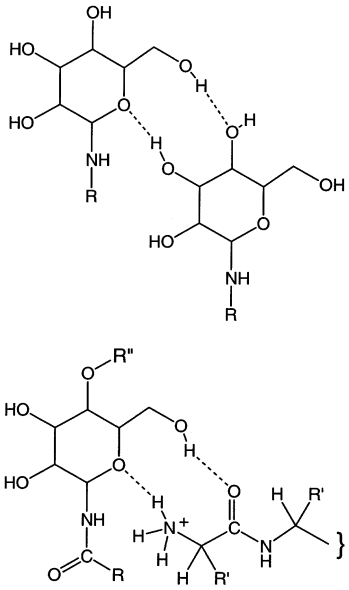
Fig. 5. Molecular packing in **11**.

10, although somewhat less weight can be given to the hydrogen positions in **10** than to those in the other structures (see Section 3).

The same hydrogen-bond pattern found in **7**–**11** is maintained in even the 'different' structure **12**, for which the data support a structure with two independent molecules in the asymmetric unit (as in **4**) as opposed to a cell half the size and a structure with a disordered aryl ring. If the torsional angles to the aryl rings had been the same, with little additional change the molecules would have been translationally related instead of crystallographically independent and **12** would have been isostructural with **7**–**11**.

Even such a potentially disruptive exchange as a nitro group for a hydrogen atom in **11** causes no significant change in the packing arrangement. In **11** the nitro group is isolated from the hydrogen-bonding pattern established by the monosaccharide hydroxyl groups, so its presence in or absence from the structure has little effect. Although we have not investigated its optical properties, compound **11** is a potential nonlinear optical material. Connecting a *p*-nitroaniline group to one enantiomer of a monosaccharide to form the optically active glycosylamine is a strategy guaranteed to place this polar group in the noncentrosymmetric crystalline environment required for nonlinear optical applications.[32] The second harmonic generation efficiency of a related compound, *N*-(4-nitrophenyl)arabinopyranosylamine, is reported to be ten times that of urea.[33] Optical properties and other physical properties of **11** might be modified in controlled fashion by cocrystallizing **11** with one or more of its isostructural analogues **7**–**10**.

The tendency toward isostructuralism among these mannopyranosylamines and galactopyranosylamines reflects the strength of the hydrogen-bonding interactions linking monosaccharide moieties, interactions characteristic of the sugar and so important in determining the packing arrangement that they may be preserved from compound to compound regardless of changes in the structure of the aglycone. Even in 2-nitrophenyl 1-thio-β-D-galactopyranoside,[30] a structure different (orthorhombic instead of monoclinic, a sulfur-



Scheme 2. H-bonding interaction observed in **1**–**6** (top); hypothetical corresponding interaction between a glycoprotein and an N-terminal peptide residue (bottom).

for-nitrogen exchange, and a different ring position for the nitro group) from **7**–**12**, three of the four hydroxyl groups serve as H-bond donors to the same atoms as in **7**–**12** and with the same symmetry relationship (translational for O-2–H-2···O-6; screw-axial for O-4–H-4···O-3 and O-6–H-6···O3). In the mannopyranosylamine series **1**–**6**, the O-3–H···O-5 and O-6–H···O-4 contacts between translationally related molecules appear to be especially favorable interactions, being found in every structure examined and in different packing arrangements. This raises the possibility that other molecules with suitably positioned hydrogen-bond donor and acceptor atoms might interact with a mannopyranosylamine in this same manner preferentially (Scheme 2). These small-molecule structures thus may serve as useful models in the study of molecular recognition in macromolecular systems such as glycoproteins and proteoglycans.

3. Experimental

Preparation of N-*aryl*-β-D-*glycopyranosylamines*.—Compounds **1**–**12** were prepared by combining D-mannose or D-galactose (0.3 g) with an equimolar amount of aniline or substituted aniline in 15 mL of EtOH to which 2–3 drops of glacial HOAc had been added. Crystals suitable for X-ray analysis could be obtained by concentrating the solution to approximately 8 mL and recrystallizing the powdery solid thus obtained from EtOH or by simply allowing the reaction mixture to slowly evaporate to dryness. Compound **1** was obtained as thin colorless plates, mp 178–180 °C (lit. 166–167 °C;[34] **2** as colorless flat needles, mp 171–173 °C (lit. 187 °C[16], 168–169 °C[34]); **3** as colorless prisms, mp 195–198 °C; **4** as colorless sword-shaped crystals, mp 160 °C (lit. 150–152 °C[34]); **5** as colorless plates, mp 194–196 °C; **6** as fine colorless needles, mp 171–174 °C (lit. 167 °C[16]); **7** as colorless needles, mp 155 °C (lit. 150 °C[16]); **8** as colorless needles, mp 193–196 °C (lit. 184 °C[16]); **9** as colorless rods, mp 170–173 °C; **10** as pale yellow needles, mp 162–164 °C; **11** as pale yellow, sword-shaped crystals, mp 212–214 °C (lit. 219 °C[15]); and **12** as colorless needles, mp 152 °C (lit. 161 °C[16]).

Like those of the analogous *N*-phenylmannopyranosylamine,[20] crystals of **7** were found upon examination under the microscope to be hollow with solvent trapped inside. Attempts to trim these crystals to a size suitable for X-ray data collection caused the solvent to bubble and flow out of the crystal. An intact, untrimmed crystal of **7** was used for data collection; the existence of the solvent channel did not appear to affect the quality of the structure determination significantly.

X-ray crystal structure determinations.—A summary of the crystal data, data collection parameters, and refinement results is given in Table 4. In all twelve structures the non-hydrogen atoms were refined anisotropically. The best crystals of **1**, **9**, and **10** that could be obtained for crystallographic analysis were very small and thin, and the analyses suffered from the combination of small crystal size and large contribution of the halogen atom to the scattering. Attempts to refine the positional parameters of the hydrogen atoms in these circumstances led to unreasonably short O–H bond lengths. Subsequently for **1** and **9** the C–H hydrogen atoms were placed in calculated positions and the O–H and N–H hydrogen atoms were left in difference map positions. For **10** the most reasonable results

Table 4
Crystal data, data collection parameters, and refinement results for **1**–**12**

	1	**2**	**3**
Formula	$C_{12}H_{16}BrNO_5$	$C_{13}H_{19}NO_5$	$C_{12}H_{16}ClNO_5$
Formula weight	334.17	269.30	289.72
Crystal dimensions (mm)	$0.24\times0.22\times0.04$	$0.50\times0.16\times0.08$	$0.36\times0.20\times0.08$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	6.537(1)	6.444(1)	6.472(1)
b (Å)	6.950(1)	6.752(1)	6.8199(9)
c (Å)	14.799(1)	15.530(1)	15.008(1)
β (°)	101.26(1)	96.56(1)	101.510(9)
V (Å^3)	659.5(2)	671.3(2)	649.2(1)
Z	2	2	2
D_{calcd} (g cm^{-3})	1.683	1.332	1.482
$F(000)$	340	288	304
μ(Cu K$_\alpha$) (cm^{-1})	44.27	8.59	27.82
$2\theta_{max}$ (°)	140.3	140.2	140.3
Measured reflections	2760	2792	2571
Unique reflections	1274	1274	1165
R_{int}	0.034	0.025	0.031
Observed reflections [$I>0.00\sigma(I)$]	2325	2327	2114
Variables	171	187	220
Trans. coefficients	0.6552–1.0000	0.9314–1.0000	0.6899–1.0000
Secondary extinction[35]		3.33227×10^{-5}	1.20861×10^{-5}
Min, max in final difference map (e Å^{-3})	−0.92, 0.58	−0.19, 0.18	−0.44, 0.38
R; wR	0.065; 0.040	0.043; 0.029	0.051; 0.034

	4	**5**	**6**
Formula	$C_{13}H_{19}NO_6$	$C_{12}H_{16}ClNO_5$	$C_{13}H_{19}NO_5$
Formula weight	285.30	289.72	269.30
Crystal dimensions (mm)	$0.56\times0.32\times0.10$	$0.44\times0.28\times0.06$	$0.56\times0.14\times0.12$
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$C2$	$P2_12_12_1$
a (Å)	12.947(2)	14.8155(6)	11.458(3)
b (Å)	6.7299(9)	5.6762(7)	20.048(5)
c (Å)	15.7880(9)	17.363(1)	6.032(3)
β (°)	95.217(7)	110.447(5)	
V (Å^3)	1369.9(3)	1368.2(2)	1385.7(6)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.383	1.406	1.291
$F(000)$	608	608	576
μ (Cu K$_\alpha$) (cm^{-1})	9.31	26.40	8.32
$2\theta_{max}$ (°)	140.2	140.2	140.1
Measured reflections	5491	2744	3035
Unique reflections	2621	1320	1519
R_{int}	0.017	0.028	0.029
Observed reflections [$I>0.00\sigma(I)$]	4795	2362	2538
Variables	391	180	188
Trans. coefficients	0.8716–1.0000	0.6645–1.0000	0.9654–1.0000
Secondary extinction[35]		9.29949×10^{-6}	2.60792×10^{-6}
Min, max in final difference map (e Å^{-3})	−0.23, 0.26	−0.29, 0.28	−0.21, 0.26
R; wR	0.059; 0.035	0.046; 0.036	0.058; 0.035

	7	**8**	**9**
Formula	$C_{12}H_{17}NO_5$	$C_{12}H_{16}ClNO_5$	$C_{12}H_{16}BrNO_5$
Formula weight	255.27	289.72	334.17
Crystal dimensions (mm)	$0.68\times0.14\times0.14$	$0.36\times0.07\times0.06$	$0.56\times0.12\times0.10$
Crystal system	monoclinic	monoclinic	monoclinic

Table 4 (*Continued*)

Space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	4.8224(6)	4.781(1)	4.7676(6)
b (Å)	8.7142(8)	8.5224(6)	8.5661(6)
c (Å)	14.0550(6)	15.9336(7)	16.1373(6)
β (°)	96.377(7)	96.955(9)	96.694(8)
V (Å^3)	586.99(8)	644.5(1)	654.55(10)
Z	2	2	2
D_{calcd} (g cm^{-3})	1.444	1.493	1.695
$F(000)$	272	304	340
μ(Cu K$_\alpha$) (cm^{-1})	9.04	28.18	44.61
$2\theta_{max}$ (°)	140.2	140.2	140.1
Measured reflections	2515	2731	2838
Unique reflections	1115	1207	1255
R_{int}	0.017	0.032	0.030
Observed reflections [$I>0.00\sigma(I)$]	2073	2243	2336
Variables	178	187	172
Trans. coefficients	0.8962–1.0000	0.9269–1.0000	0.8984–1.0000
Secondary extinction[35]	1.17627×10^{-4}	7.55625×10^{-6}	3.27365×10^{-5}
Min, max in final difference map (e Å^{-3})	−0.14, 0.16	−0.21, 0.22	−0.57, 0.27
R; wR	0.035; 0.035	0.043; 0.022	0.034; 0.033
	10	**11**	**12**
Formula	$C_{12}H_{16}INO_5$	$C_{12}H_{16}N_2O_7$	$C_{13}H_{19}NO_5$
Formula weight	381.17	300.27	269.30
Crystal dimensions (mm)	$0.44\times0.06\times0.06$	$0.56\times0.28\times0.07$	$0.48\times0.13\times0.12$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	4.768(2)	4.845(2)	9.628(1)
b (Å)	8.655(2)	8.361(1)	8.5347(6)
c (Å)	16.438(1)	16.032(1)	16.0070(8)
β (°)	95.85(2)	97.74(2)	97.498(6)
V (Å^3)	674.8(2)	643.5(2)	1304.0(2)
Z	2	2	4
D_{calcd} (g cm^{-3})	1.876	1.550	1.372
$F(000)$	376	316	576
μ(Cu K$_\alpha$) (cm^{-1})	188.14	11.11	8.84
$2\theta_{max}$ (°)	140.2	140.2	140.3
Measured reflections	2759	2703	5194
Unique reflections	2264	1193	2440
R_{int}	0.026	0.029	0.031
Observed reflections [$I>0.00\sigma(I)$]	2254	2208	4537
Variables	177	237	373
Trans. coefficients	0.5329–1.0000	0.8451–1.0000	0.9412–1.0000
Secondary extinction[35]			1.25965×10^{-5}
Min, max in final difference map (e Å^{-3})	−0.95, 1.23	−0.17, 0.13	−0.28, 0.22
R; wR	0.065; 0.048	0.036; 0.035	0.056; 0.032

For all twelve structures: $T=298$ K; diffractometer: Rigaku AFC6S; radiation: Cu K$_\alpha$; $\lambda=1.54178$ Å; cell determination: 25 reflections (24 for **7**), $45<2\theta<50°$; data collection: MSC/AFC control software;[36] scan mode: $\omega/2\theta$; structure solution: SHELXS86;[37] structure refinement: teXsan software package;[38] decay correction: none for **1**, **3**–**6**, **8**–**12**; 2.75% for **2**, 1.46% for **7**; absorption corrections: psi scans;[39] figures: ORTEPII;[22] $R=\Sigma\big||F_{obs}|-|F_{calc}|\big|/\Sigma|F_{obs}|$; $wR=[(\Sigma w(|F_{obs}|-|F_{calc}|)^2/\Sigma wF_{obs}^2]^{1/2}$; $w=4F_{obs}^2/\sigma^2(F_{obs}^2)$; $R_{int}=\Sigma\Sigma\big|\langle F_i^2\rangle-F_{ij}^2\big|/\Sigma m\langle F_i^2\rangle$.

were obtained by placing C–H hydrogen atoms in atoms in calculated positions, refining the positional parameters of the O-2 and O-6 hydrogen atoms, and leaving the N–H and remaining O–H hydrogen atoms in difference map positions. The relatively large electron-density peaks remaining in the difference map were associated with the iodine atom. In **5** the O-2

and O-4 hydrogen atoms were left in difference map positions, the positional parameters of the remaining O–H hydrogen atoms and the N–H hydrogen atom were refined, and the C–H hydrogen atoms were placed in calculated positions. In **2**, **4**, **6**, **7**, **8**, and **12**, the positional parameters of the O–H and N–H hydrogen atoms were refined and the C–H hydrogen atoms were placed in calculated positions. In **3** and **11**, the positional parameters of all of the hydrogen atoms were refined.

4. Supplementary material

Full crystallographic details for **1**–**12** (excluding structure features) have been deposited with the Cambridge Crystallographic Data Centre. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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