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Crystal structure and solid-state ^{13}C NMR analysis of *N*-*o*-, *N*-*m*- and *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamines, and their *N*-acetyl derivatives

Andrzej Temeriusz,[a,*] Tomasz Gubica,[a] Paulina Rogowska,[a]
Katarzyna Paradowska[b] and Michał K. Cyrański[a]

[a] *Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warszawa, Poland*
[b] *Department of Physical Chemistry, Faculty of Pharmacy, Medical Academy, Banacha 1, 02-097 Warszawa, Poland*

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Abstract—The X-ray diffraction analysis of *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**), *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamines, *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamines, and their *N*-acetyl derivatives was performed. The sugar moieties always adopt $^4C_1$ conformations, however, due to crystal packing forces they are always slightly distorted. It was found that except *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**), none of the glucopyranosylamines studied in this paper form strong hydrogen bonds in the crystal lattice. Additionally, (**5**) crystallizes with a molecule of water, which occupies a special crystallographic position (on the twofold axis) and links two sugar molecules by hydrogen bonds. The CP MAS NMR spectra confirmed the presence of the intermolecular hydrogen bond involving the molecule of water in (**5**). Moreover, it was proved that in (**1**) an intramolecular hydrogen bond is formed between the glycosidic linkage and the nitro group.

Keywords: Glucopyranosylamines; Crystal structure; ^{13}C NMR analysis; Solid-state NMR

1. Introduction

This paper is a continuation of our previous work focused on structural studies on some of the *N*-nitrophenylglycopyranosylamines, the derivatives of aldopentoses.[1] Glycosylamines have become the subject of interest because of their biochemical properties, for example, the application in sugar enzymology as inhibitors of glycosidases.[2]

Nitrophenylglucopyranosylamines are also of interest owing to their electrochemical properties. Electrochemical behaviours of the nitro aromatic compounds is well known[3–7] but the influence of the second substituent in nitrobenzene on electrochemical properties is not well described. Núñez-Vergara et al.[8] have investigated the influence of the methoxy group on electroreduction of the nitro group of all isomeric nitroanisoles, explaining different behaviour of isomeric nitroanisoles by electronic and steric effects of the methoxy group. We have investigated electrochemical properties of *N*-nitrophenylglucopyranosylamines. Electroreduction of compound (**1**) was not comparable to electroreduction of *o*-nitroanisole (unpublished results). This different electrochemical behaviour is caused by the formation of a hydrogen bond between N–H and the nitro group in (**1**), which stabilized the coplanarity between the nitro group and the aromatic ring, and therefore it facilitates the positive resonance effect of nitrogen glycosidic atom in the *ortho* position. In the case of *o*-nitroanisole and compound (**4**) the loss of the above-mentioned coplanarity inhibits the resonance effect of this nitrogen atom.

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* Corresponding author. Fax: +48 22 822 5996; e-mail: atemer@chem.uw.edu.pl

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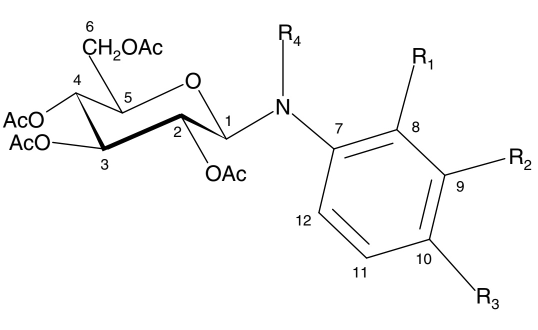
2. Results and discussion

N-Nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamines and their *N*-acetyl derivatives presented in Scheme 1 were prepared by acetylation of appropriate *N*-nitrophenyl-D-glucopyranosylamines with acetic anhydride in pyridine, while the N-acetylation was performed at high temperature by acetic anhydride with the addition of a catalytic amount of anhydrous zinc chloride. The appropriate crystals of compounds (**1**)–(**6**) for X-ray investigations were obtained by slow evaporation from ethanol. Crystal data and structural refinement are specified in Table 1, the selected torsion angles for (**1**)–(**6**) are given in Table 2, whereas the molecular structures are shown in Figures 1 and 2. Except for *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**), none of the glucopyranosylamines studied in this paper formed strong hydrogen bonds in the crystal lattice, as no short interactions were observed. The molecules were rather stabilized by van der Waals interactions and possibly by weak intermolecular hydrogen bonds, involving the oxygen atoms from the acetyl groups or from the sugar ring from one side, and CH fragments (both from the sugar ring and methyl groups) from the other one. The closest intermolecular C–H···O interactions were 2.35–2.6 Å (C···O distance 3.12–3.51 Å). *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**) crystallized with a molecule of water, which occupied a special crystallographic position (on the twofold axis) and linked two sugar molecules by hydrogen bonds, as shown in Figure 3. Those hydrogen bonds were quite strong and the distance between O-100–H···O-131 was 1.907 Å (O···O is 2.769(2) Å). In *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**) due to close proximity of the –NH and $-NO_2$ groups, an additional intramolecular hydrogen bond was formed with the N-1–H···O-81 distance of 1.984 Å (N-1···O-81 is 2.647(3) Å). In consequence, the nitro group was only moderately twisted with respect to the phenyl ring, as compared with its *N*-acetyl analogue (**4**). The C-7–C-8–N-8–O-81, C-9–C-8–N-8–O-81, C-7–C-8–N-8–O-82 and C-9–C-8–N-8–O-82 torsion angles were −14.0(4), 167.1(2), 167.1(2) and −11.8(3), respectively, in the former case and −42.4(4), 137.2(3), 139.6(3) and −40.8(3), respectively, in the latter. Obviously, the serious distortion from coplanarity in compound (**4**) was caused by steric hindrance of the acetyl group at nitrogen. A sharp deviation from coplanarity of the nitro group with the phenyl ring was also observed in *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**2**), where the respective torsion angles were 21.2(4), −158.1(3), −157.7(3), 23.1(4). In fact, such flexibility of the nitro group did not seem to be unusual, and it was recently observed in *o*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside and *o*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[9] (where the distortion from coplanarity of about 40–55° resulted from steric interactions between the nitro group and sugar moiety) and in *p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[9] (where the distortion of circa 14° was associated with weak intermolecular interactions in the crystal lattice). In the case of the other glucopyranosylamines discussed in this paper, the nitro group was never coplanar with the phenyl ring, however the twist was less than 10°. These observations strongly support the view[10,11] that the nitro group does not conjugate effectively with the benzene ring, and even weak intermolecular interactions in the crystal lattice may efficiently distort it from planarity.



1 $R_1 = NO_2, R_2 = R_3 = R_4 = H$
2 $R_2 = NO_2, R_1 = R_3 = R_4 = H$
3 $R_3 = NO_2, R_1 = R_2 = R_4 = H$
4 $R_1 = NO_2, R_2 = R_3 = H, R_4 = OAc$
5 $R_2 = NO_2, R_1 = R_3 = H, R_4 = OAc$
6 $R_3 = NO_2, R_1 = R_2 = H, R_4 = OAc$

Scheme 1.

The most significant differences resulting from different packing forces concerned the torsion angles of the side chains in respect of the sugar ring: C-1–C-2–O-21–C-22, C-3–C-2–O-21–C-22, C-2–C-3–O-31–C-32, C-4–C-3–O-31–C-32, C-3–C-4–O-41–O-42, C-5–C-4–O-41–O-42, C-4–C-5–C-6–O-61, O-5–C-5–C-6–O-61 and the torsion angle of the side chains C-5–C-6–O-61–C-62 and C-7–N-1–C-13–O-131, which might vary within a wide range. Moreover, the *N*-acetyl, *N*-nitrophenyl-glucopyranosylamines differed significantly from the parent molecules in the torsion angles O-5–C-1–N-1–C-7. The mean values for those angles varied between −72.9 to −80.4 for (**1**), (**2**), (**3**), and 39.1–60.7 for (**4**), (**5**) and (**6**). Similarly, the torsion angle C-2–C-1–N-1–C-7 varied between 158.3–169.8 for (**1**), (**2**), (**3**), and between −60.3 to −80.6 for (**4**), (**5**) and (**6**).

The sugar moieties always adopted $^4C_1$ conformations, however, due to crystal packing forces they were always slightly distorted. The most significant deviations were found for compounds (**1**) and (**3**), as quantified by the Cremer–Pople Θ puckering parameters.[12,13] Θ Was equal to 10.3° and 10.6°, while the other puckering parameters Q and φ were equal to 0.578, 303.1, 0.601

Table 1. Crystal data and structure refinement for *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**), *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**2**), *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**3**), *N*-acetyl, *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**4**), *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**) and *N*-acetyl, *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**6**)

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{20}H_{24}N_2O_{11}$	$C_{20}H_{24}N_2O_{11}$	$C_{20}H_{24}N_2O_{11}$	$C_{22}H_{26}N_2O_{12}$	$C_{22}H_{26}N_2O_{12}\cdot 0.5H_2O$	$C_{22}H_{26}N_2O_{12}$
Colour	Yellow	Yellow	Yellow	White	White	White
Formula weight	468.4	468.4	468.4	510.5	519.5	510.5
Temperature (K)	100	100	100	100	100	100
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$	$C2$	$P2_12_12_1$
Unit cell dimensions						
a (Å)	7.016(1)	10.641(1)	5.423(1)	8.862(2)	21.608(4)	6.993(1)
b (Å)	13.241(3)	8.030(1)	22.751(2)	7.864(2)	8.031(2)	13.690(2)
c (Å)	23.479(5)	13.061(1)	9.404(1)	18.564(4)	15.702(3)	25.476(3)
β (°)	90	101.89(1)	103.20(1)	102.65(3)	114.25(3)	90
Volume (Å^3)	2181.2(8)	1092.0(2)	1129.5(2)	1262.3(4)	2484.4(9)	2438.8(5)
Z (molecules/cell)	4	2	2	2	4	4
$D_{\text{calculated}}$ (Mg/m^3)	1.426	1.425	1.377	1.343	1.389	1.390
Absorption coefficient (mm^{-1})	0.118	0.118	0.114	0.111	0.115	0.115
$F(000)$	984	492	492	536	1092	1072
Crystal size (mm)	$0.35 \times 0.35 \times 0.25$	$0.35 \times 0.25 \times 0.20$	$0.35 \times 0.30 \times 0.20$	$0.30 \times 0.30 \times 0.20$	$0.4 \times 0.35 \times 0.25$	$0.40 \times 0.30 \times 0.25$
Limiting indices	$-8 \leqslant h \leqslant 7$, $-15 \leqslant k \leqslant 15$, $-27 \leqslant l \leqslant 27$	$-12 \leqslant h \leqslant 12$, $-9 \leqslant k \leqslant 8$, $-15 \leqslant l \leqslant 15$	$-6 \leqslant h \leqslant 6$, $-27 \leqslant k \leqslant 26$, $-11 \leqslant l \leqslant 11$	$-9 \leqslant h \leqslant 10$, $-9 \leqslant k \leqslant 9$, $-22 \leqslant l \leqslant 21$	$-25 \leqslant h \leqslant 25$, $-7 \leqslant k \leqslant 9$, $-8 \leqslant l \leqslant 8$	$-8 \leqslant h \leqslant 7$, $-16 \leqslant k \leqslant 16$, $-30 \leqslant l \leqslant 30$
Reflections collected/ unique reflections	16699/3829 [$R_{\text{int}} = 0.0691$]	8250/3120 [$R_{\text{int}} = 0.0596$]	8575/3888 [$R_{\text{int}} = 0.0253$]	9436/3916 [$R_{\text{int}} = 0.0559$]	9409/3380 [$R_{\text{int}} = 0.0270$]	18692/4293 [$R_{\text{int}} = 0.1369$]
Data/parameters	3829/307	3120/307	3888/307	3916/331	3380/337	4293/331
Goodness-of-fit on F^2	0.848	0.759	0.951	0.982	0.973	0.978
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.0602$	$R_1 = 0.0386$, $wR_2 = 0.0423$	$R_1 = 0.0278$, $wR_2 = 0.0546$	$R_1 = 0.0430$, $wR_2 = 0.0959$	$R_1 = 0.0286$, $wR_2 = 0.0586$	$R_1 = 0.0517$, $wR_2 = 0.1141$
R indices (all data)	$R_1 = 0.0590$, $wR_2 = 0.0655$	$R_1 = 0.0731$, $wR_2 = 0.0479$	$R_1 = 0.0334$, $wR_2 = 0.0564$	$R_1 = 0.0534$, $wR_2 = 0.1023$	$R_1 = 0.0332$, $wR_2 = 0.0602$	$R_1 = 0.0621$, $wR_2 = 0.1198$
Extinction coefficient	0.0032(4)	0.0072(4)	0.011(1)	0.014(2)	0.0044(4)	0.0000(14)
Largest differences peak and hole (e/A^{-3})	0.157 and −0.178	0.189 and −0.198	0.128 and −0.129	0.628 and −0.198	0.182 and −0.193	0.263 and −0.308

Table 2. Selected torsion angles for *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**), *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**2**), *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**3**), *N*-acetyl, *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**4**), *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**) and *N*-acetyl, *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**6**)

Torsion angle	Compound					
	1	**2**	**3**	**4**	**5**	**6**
O-5–C-1–C-2–O-21	167.2(2)	−177.5(2)	173.4(1)	176.1(2)	−179.3(1)	174.5(2)
N-1–C-1–C-2–C-3	169.3(2)	−178.1(3)	174.2(1)	179.1(2)	−177.4(1)	175.6(2)
C-1–C-2–O-21–C-22	108.8(2)	145.2(3)	96.7(2)	133.5(2)	151.0(2)	114.6(2)
C-3–C-2–O-21–C-22	−130.0(2)	−98.1(3)	−142.2(1)	−108.9(2)	−91.9(2)	−127.5(3)
C-4–C-3–O-31–C-32	106.8(2)	149.2(2)	129.0(2)	97.1(3)	148.4(2)	124.8(2)
C-2–C-3–O-31–C-32	−135.1(2)	−92.8(3)	−110.1(2)	−141.7(2)	−93.0(2)	−115.4(3)
C-3–C-4–O-41–C-42	111.1(2)	120.7(3)	126.5(1)	98.0(3)	114.4(2)	141.3(2)
O-5–C-5–C-6–O-61	−73.3(2)	−63.2(3)	71.4(2)	−64.4(3)	−72.1(2)	175.0(2)
C-4–C-5–C-6–O-61	45.8(3)	56.6(3)	−169.9(1)	57.2(3)	47.3(2)	−68.1(3)
C-5–C-6–O-61–C-62	−138.1(2)	171.0(3)	131.9(2)	157.5(2)	−122.9(2)	172.4(2)
O-5–C-1–N-1–C-7	−80.4(3)	−84.7(3)	−72.9(2)	42.2(3)	60.7(2)	39.1(3)
C-2–C-1–N-1–C-7	158.7(2)	158.3(3)	169.8(1)	−77.0(3)	−60.3(2)	−80.6(3)
C-1–N-1–C-7–C-8	−179.9(2)	19.7(5)	16.7(2)	−79.4(3)	83.2(2)	98.6(3)
C-1–N-1–C-7–C-12	−1.2(4)	−162.1(3)	−165.3(2)	98.3(3)	−98.2(2)	−82.1(3)
C($x-1$)–C(x)–N(x)–O(x1)	−14.0(4)	21.2(4)	5.2(2)	−42.4(4)	7.4(3)	−6.5(4)
C($x+1$)–C(x)–N(x)–O(x1)	167.1(2)	−158.1(3)	−174.7(2)	137.2(3)	−172.2(2)	176.8(3)
C($x-1$)–C(x)–N(x)–O(x2)	167.1(2)	−157.7(3)	−175.2(2)	139.6(3)	−171.8(2)	172.2(3)
C($x+1$)–C(x)–N(x)–O(x2)	−11.8(3)	23.1(4)	5.0(2)	−40.8(3)	8.7(3)	−4.5(4)
C-7–N-1–C-7–O-131				−172.0(3)	0.0(2)	−178.7(3)
C-1–N-1–C-7–O-131				−5.7(4)	−6.3(3)	−7.9(4)
C-1–N-1–C-7–C-132				9.2(4)	0.3(3)	2.4(4)
C-1–N-1–C-13–C-132				175.4(3)	174.0(2)	173.3(2)
O-5–C-1–N-1–C-13				−124.6(2)	−113.1(2)	−132.0(3)
C-2–C-1–N-1–C-13				116.1(3)	126.0(2)	108.4(3)
C-13–N-1-C-7–C-8				87.0(3)	−103.2(2)	−90.4(3)
C-13–N-1-C-7–C-12				−95.4(3)	75.4(2)	88.9(3)

x Concerns the enumeration of atoms in respect to the label of the nitrogen atom in the nitro group.

and 353.0, respectively, for compound (**1**) and (**3**). For comparison Θ was equal to 9.3°, 8.5°, 4.6° and 3.5°, respectively, for (**2**), (**4**), (**5**) and (**6**), whereas Q and φ were equal, respectively, to 0.606 and 54.6 for (**2**), 0.573 and 40.6 for (**4**), 0.638 and 7.8 for (**5**) and 0.603 and 326.1 for (**6**).

The one- and two-dimensional ^{1}H and ^{13}C NMR spectra for $CDCl_3$ solutions of (**1**)–(**6**) were recorded and analyzed in order to obtain reliable assignment of the ^{13}C resonances. The ^{13}C spectra for solids were recorded using the cross-polarization (CP) magic angle spinning (MAS) technique, and the spectra of (**1**) (Fig. 4) and (**5**) (Fig. 5) are illustrated in their respective figures. The ^{13}C NMR chemical shifts for three D-glucopyranosylamines (**1**), (**2**), (**3**) and three *N*-acetyl-D-glucopyranosylamines (**4**), (**5**), (**6**) are collected in Table 3.

The ^{13}C CP MAS spectra were well resolved and the bands of resonances of aromatic carbons and sugar carbons could be recognized immediately. The resonances of C-1 and C-7 carbons could be identified since they were affected by the ^{13}C–^{14}N residual dipolar coupling and therefore were broader and/or splitted into asymmetric doublets.[14,15] Detailed assignments of the CP MAS spectra were made on the basis of liquid-state ones. However, some solid-state resonances had their chemical shifts significantly different from their liquid-state counterparts. The differences $\Delta = \delta_{\text{solid}} - \delta_{\text{solution}} > 1$ ppm (given in Table 3) could result from conformational effects and/or intermolecular interactions.

The molecules (**1**)–(**6**) were conformationally flexible, and rotamers arising from the rotation around the C-1–N glycosidic bonds could be expected. Due to the frozen orientation of the aromatic ring in the solid phase, the differences Δ from −4.0 to +3.5 ppm were observed for aromatic carbons. The sugar fragment was also flexible in solution, locked conformation of C-6–OCH_2– in solid state resulted in significant differences for C-6 [−2.0 in (**5**), +3.8 in (**6**)].

The amino group did not participate in intermolecular hydrogen bonds with the parent molecule for steric reasons. An intramolecular N–H···O=N hydrogen bond occurred in (**1**); carbons C-7 and C-8 were within the cycle but only a small deshielding of 1.2 ppm was observed for C-7. In the crystals of (**5**), intermolecular C=O···HOH hydrogen bonds were present and the water molecule served as a link between the two symmetry related molecules. The chemical shifts of the respective C=O carbons (involved in hydrogen bonds) were 173.1 and 172.1 ppm whereas in all other compounds δ were within 167.0–170.0 ppm.

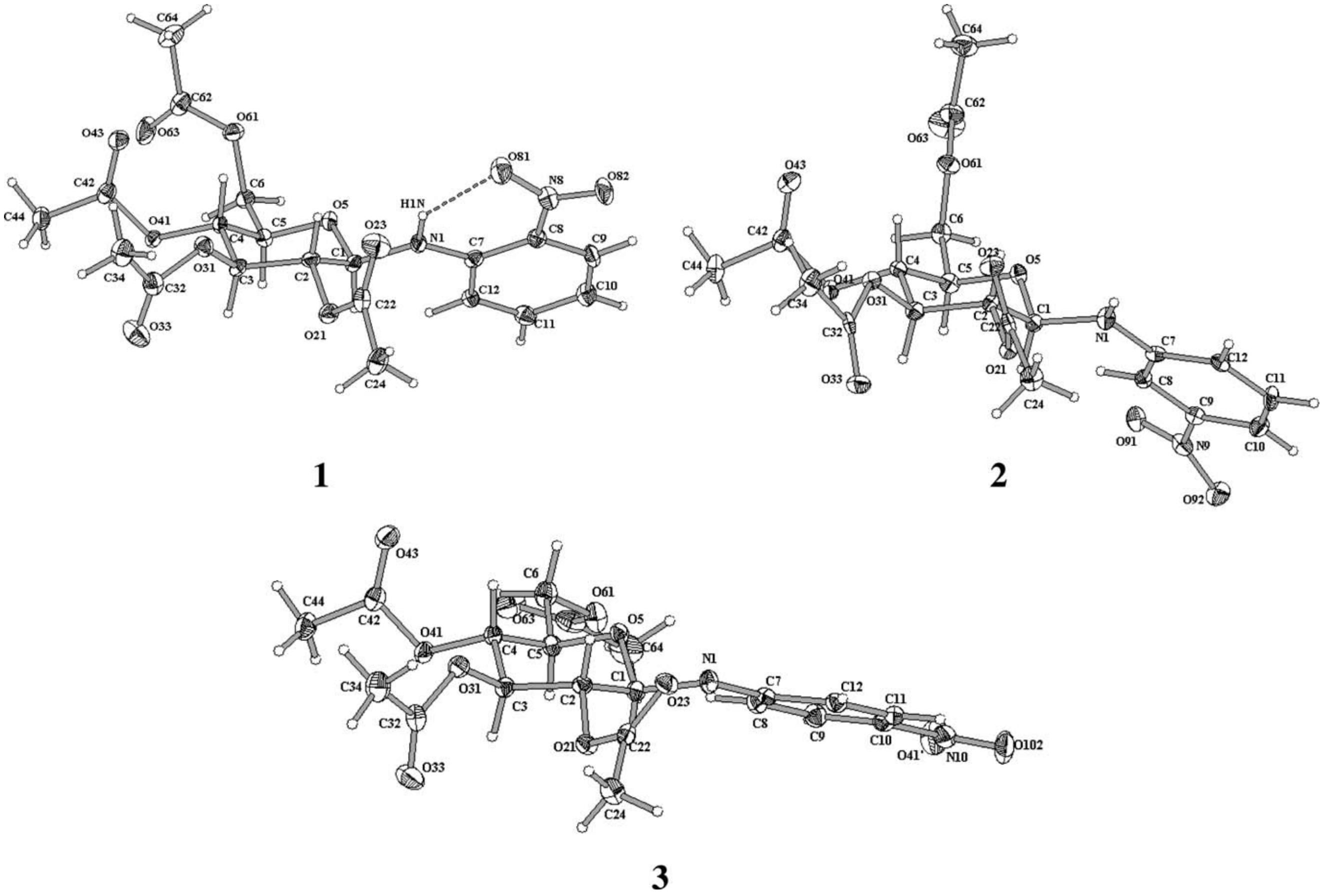


Figure 1. ORTEP scheme and atom numbering of *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**), *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**2**) and *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**3**). Displacement ellipsoids are drawn at the 50% probability level.

The bulky acetyl group induced geometrical changes within that structural fragment, such as the twisting of the aromatics ring, or different angles at the nitrogen atom (–N–H with respect to –N–Ac). Substantial chemical shift differences between *N*-nitrophenyl, *N*-acetyl and *N*-nitrophenyl compounds were observed in both phases, the effects were most significant for C-8 and C-12 (15–17 ppm).

3. Experimental

3.1. A general procedure for synthesis of *N*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamines (1)–(3)

To a solution of the appropriate *N*-nitrophenylglucopyranosylamine[16–18] (0.01 mol) in dry pyridine (25 mL), Ac_2O (25 mL) was added at 0 °C. The obtained solutions were left at 0 °C overnight. Afterwards, the reaction mixtures were poured into crushed ice and left until crystalline raw products were formed. The obtained crystals were washed several times with water and air-dried. The compounds (**1**)–(**3**) were purified by crystallization from ethanol.

3.2. *N*-*o*-Nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (1)

This compound was prepared according to the general procedure. Yellow crystals, yield, 85%; mp 184.5–185.5 °C; $[\alpha]_D^{20}$ −71.0 ($CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.43 (d, 1H, $J_{N,1} = 7.5$ Hz, H–N), 8.20 (dd, 1H, $J_{9,10} = 8.5$ Hz, $J_{9,11} = 1.5$ Hz, H-9), 7.51 (td, 1H, $J_{10,11} = 8.0$ Hz, $J_{11,12} = 8.5$ Hz, H-11), 6.96 (d, 1H, $J_{10,12} = 1.5$ Hz, H-12), 6.90 (td, 1H, H-10), 5.41 (t, 1H, $J_{2,3} = 9.5$ Hz, $J_{3,4} = 9.5$ Hz, H-3), 5.27 (t, 1H, H-2), 5.15 (t, 1H, $J_{4,5} = 10.0$ Hz, H-4), 4.91 (dd, 1H, $J_{1,2} = 8.5$ Hz, H-1), 4.30 (dd, 1H, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6a), 4.15 (dd, 1H, $J_{5,6b} = 2.5$ Hz, H-6b), 3.91 (ddd, 1H, H-5), 2.08, 2.07, 2.06, 2.05 (4s, 12H, 4OAc). Anal. Calcd for $C_{20}H_{24}O_{11}N_2$: C, 51.28; H, 5.16; N, 5.98. Found: C, 51.14; H, 5.18; N, 5.93.

3.3. *N*-*m*-Nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (2)

This compound was prepared according to the general procedure. Yellow crystals, yield, 97%;

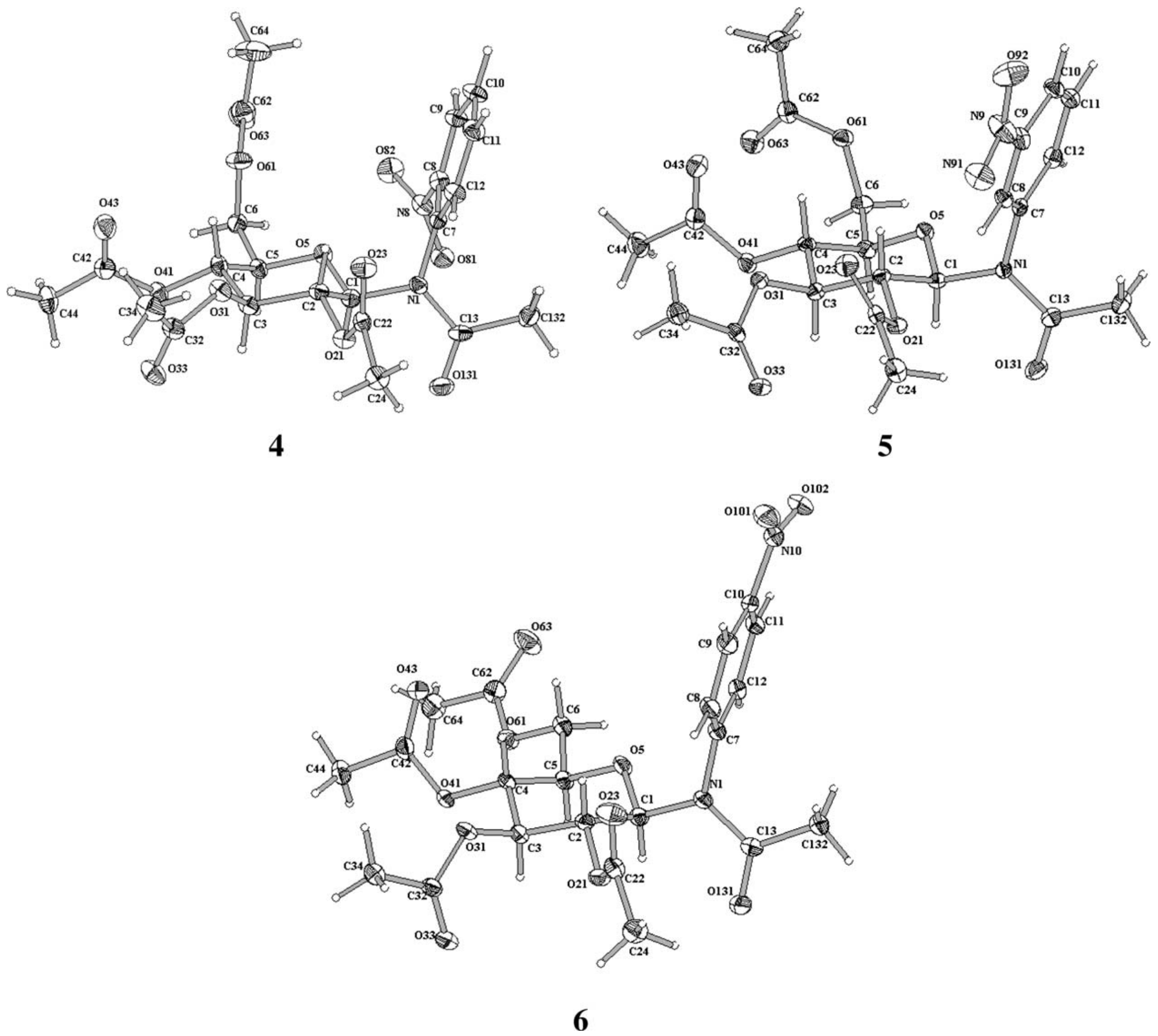


Figure 2. ORTEP scheme and atom numbering of *N*-acetyl, *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**4**), *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**) and *N*-acetyl, *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**6**). In the case of **5** the co-crystallizing water molecule omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

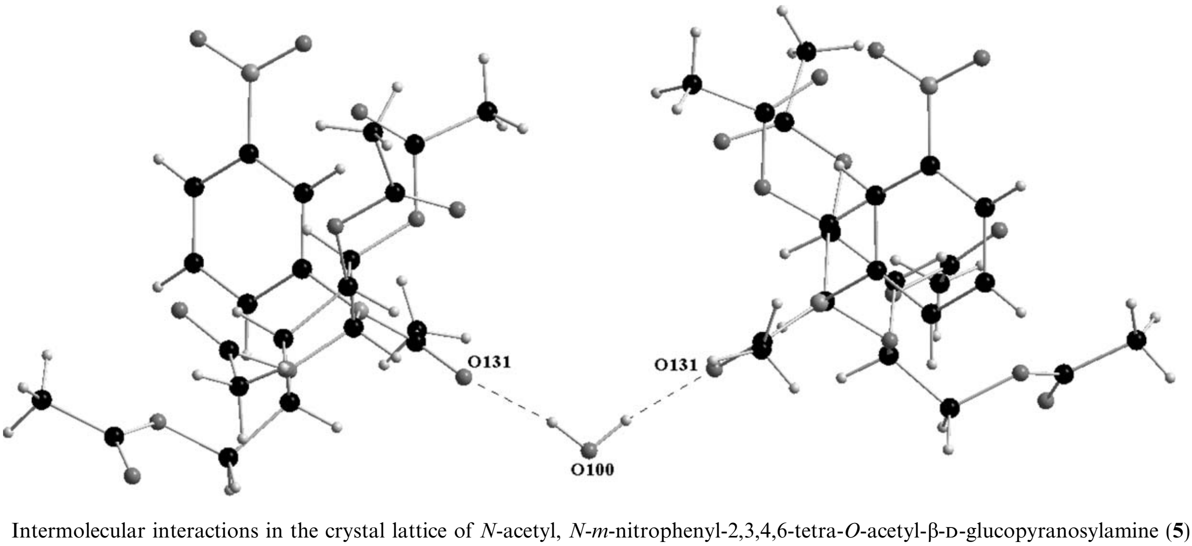


Figure 3. Intermolecular interactions in the crystal lattice of *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**).

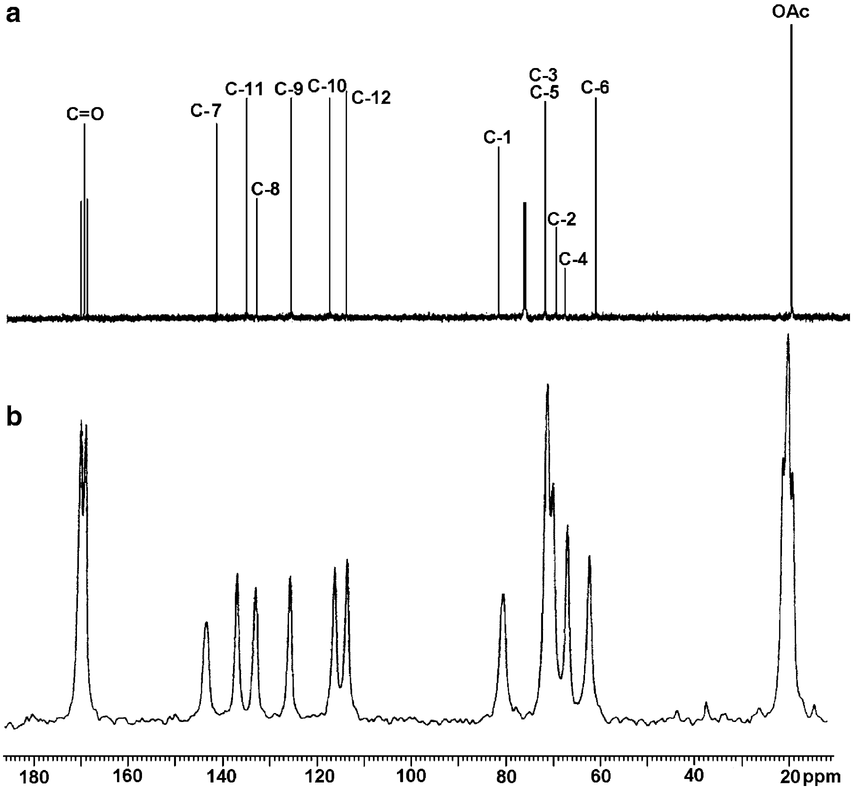


Figure 4. ^{13}C NMR spectra: *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**1**). (a) In $CDCl_3$ and (b) in solid state.

mp 135–139 °C, $[\alpha]_D^{20}$ −74.0 ($CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.69 (dd, 1H, $J_{10,11} = 8.0$ Hz, $J_{8,10} = 2.0$ Hz, H-10), 7.51 (t, 1H, $J_{8,12} = 2.5$ Hz, H-8), 7.34 (t, 1H, $J_{11,12} = 8.5$ Hz, H-11), 6.95 (dd, 1H, H-12), 5.41 (t, 1H, $J_{2,3} = 9.5$ Hz, $J_{3,4} = 9.5$ Hz, H-3), 5.23 (d, 1H, $J_{N,1} = 8.5$ Hz, H–N), 5.08 (t, 1H, $J_{4,5} = 10.0$ Hz, H-4), 5.06 (t, 1H, $J_{1,2} = 9.0$ Hz, H-2), 4.81 (t, 1H, H-1), 4.26 (dd, 1H, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 12.0$ Hz, H-6a), 4.16 (dd, 1H, $J_{5,6b} = 2.0$ Hz, H-6b), 3.92 (ddd, 1H, H-5), 2.08, 2.07, 2.07, 2.05 (4s, 12H, 4OAc). Anal. Calcd for $C_{20}H_{24}O_{11}N_2$: C, 51.28; H, 5.16; N, 5.98. Found: C, 51.30; H, 5.21; N, 5.96.

3.4. *N*-*p*-Nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (3)

This compound was prepared according to the general procedure. Yellow crystals, yield, 85%; mp 181–182 °C; $[\alpha]_D^{20}$ −95.2 ($CHCl_3$), lit.[19] mp 153–154 °C; $[\alpha]_D$ −82 (EtOH), lit.[20] mp 182–183 °C; $[\alpha]_D$ −101 ($CHCl_3$).

3.5. A general procedure for synthesis of *N*-acetyl, *N*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (4)–(6)

A mixture of appropriate compounds (**1**)–(**3**) (0.01 mol), Ac_2O (0.2 mol) and anhydrous zinc chloride (0.0005 mol) was heated at 100 °C for 60 min for compound (**4**), 40 min for **5**, and 30 min for (**6**). Then the reaction mixtures were poured into ice-water. Only raw compound (**6**) formed a crystalline product, which was washed with water, air-dried and re-crystallized from ethanol. Compounds (**4**) and (**5**) formed viscous oils, which were dissolved in chloroform and washed twice with $KHCO_3$(aq) and once with water, dried with anhydrous $MgSO_4$, evaporated to dryness and crystallized from ethanol.

3.6. *N*-Acetyl, *N*-*o*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (4)

This compound was prepared according to the general procedure. White crystals, yield, 59%; mp 131–133 °C, $[\alpha]_D^{20}$ −140.4 ($CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.93 (dd, 1H, $J_{9,10} = 8.5$ Hz, $J_{9,11} = 1.5$ Hz, H-9), 7.73 (td, 1H, $J_{10,11} = 8.0$ Hz, $J_{11,12} = 8.0$ Hz, H-11), 7.64 (td, 1H, $J_{10,12} = 1.5$ Hz, H-10), 7.45 (dd, 1H, H-12), 6.12 (d, 1H, $J_{1,2} = 9.5$ Hz, H-1), 5.26 (t, 1H, $J_{2,3} = 9.5$ Hz, $J_{3,4} = 9.5$ Hz, H-3), 4.74 (2t, 2H, $J_{4,5} = 10.0$ Hz, H-2, H-4), 3.95 (dd, 1H, $J_{5,6a} = 5.5$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6a), 3.92 (dd, 1H, $J_{5,6b} = 2.5$ Hz, H-6b), 3.81 (ddd, 1H, H-5), 2.11, 2.06, 1.99, 1.95, 1.93 (5s, 15H, 5OAc). Anal. Calcd for $C_{22}H_{26}O_{12}N_2$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.63; H, 5.19; N, 5.44.

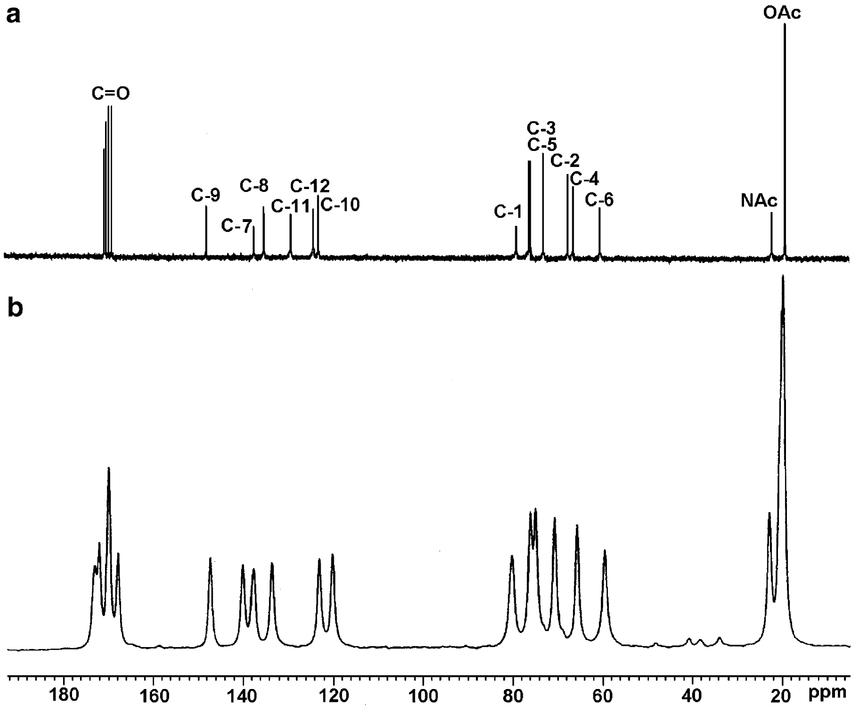


Figure 5. ^{13}C NMR spectra: *N*-acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (**5**). (a) In $CDCl_3$ and (b) in solid state.

Table 3. The ^{13}C NMR chemical shifts[a] for D-glucopyranosylamines **1**–**6**

Atom	Compound											
	1		**4**		**2**		**5**		**3**		**6**	
	δ_{solid}	δ_{liquid}	δ_{solid}	δ_{liquid}	δ_{solid}	δ_{liquid}	δ_{solid}	δ_{liquid}	δ_{solid}	δ_{liquid}	δ_{solid}	δ_{liquid}
C-1	80.9 (−1.7)	82.61	78.9	79.84	82.9	83.73	79.7	80.01	83.1	83.07	80.5	80.11
C-2	70.4	70.52	68.2 (1.2)	69.42	70.9	71.14	70.4 (1.9)	68.57	70.0 (−1.1)	71.07	67.6 (−1.1)	68.72
C-3	71.7 (−1.1)	72.76	73.9	73.66/73.75	71.6 (−1.1)	72.74	75.7 (1.6)	74.03	74.4 (2.0)	72.38	71.8 (−2.2/ −2.2)	74.02/74.05
C-4	67.3 (−1.2)	68.57	66.7	67.60	67.4 (−1.3)	68.66	65.4 (−2.1)	67.52	67.7 (−0.7)	68.38	67.6	67.58
C-5	71.7 (−1.1)	72.76	73.9	73.75/73.66	73.9 (1.3)	72.61	74.6	73.89	74.4 (1.8)	72.65	71.8 (−2.2/ −2.2)	74.05/74.02
C-6	62.5	62.02	61.2	62.00	62.9	62.13	59.4 (−2.0)	61.43	60.7 (−1.1)	61.86	65.4 (3.9)	61.54
C-7	143.5 (1.2)	142.29	130.2	129.62	148.7 (3.1)	145.57	140.2 (1.8)	138.35	151.0 (0.9)	150.08	144.8 (1.8)	142.91
C-8	133.3	134.10	150.2	149.72	104.2 (−2.9)	107.97	137.7 (1.4)	136.25	116.6 (3.5)	113.05	129.4 (−1.8)	131.27
C-9	126.2	126.67	126.5 (1.2)	125.26	151.2 (1.9)	149.27	147.5 (−1.1)	148.65	126.9 (1.0)	125.89	128.2 (3.53)	124.67
C-10	116.9 (−1.6)	118.54	130.2	130.57	114.4	114.65	120.1 (−4.0)	124.14	140.0	140.32	148.0	147.89
C-11	137.1 (1.2)	135.92	134.5	133.70	128.8 (−1.1)	129.92	133.6 (3.3)	130.33	126.9 (1.0)	125.89	128.2 (3.5)	124.67
C-12	114.2	115.01	133.9	133.17	122.9 (2.3)	120.62	123.0 (−2.3)	125.33	110.6 (−2.5)	113.05	129.4 (−1.8)	131.27

[a] Protecting groups not included.

3.7. *N*-Acetyl, *N*-*m*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (5)

This compound was prepared according to the general procedure. White crystals, yield, 91%; mp 88–94 °C; $[\alpha]_D^{20}$ +57.6 ($CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.32 (d, 1H, $J_{10,11} = 7.5$ Hz, H-11), 8.24–7.92 (br, 1H, $J_{11,12} = 8.0$ Hz, H-12), 7.65 (t, 1H, $J_{11,12} = 8.0$ Hz, H-11), 7.60–7.38 (br, 1H, H-8), 6.16 (br, 1H, H-1), 5.26 (t, 1H, $J_{2,3} = 9.5$ Hz, $J_{3,4} = 9.5$ Hz, H-3), 4.96 (t, 1H, $J_{4,5} = 10.0$ Hz, H-4), 4.57 (t, 1H, $J_{1,2} = 9.5$ Hz, H-2), 4.24 (dd, 1H, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6a), 4.20 (dd, 1H, $J_{5,6b} = 4.0$ Hz, H-6b), 3.88 (ddd, 1H, H-5), 2.08, 2.06, 2.02, 1.91, 1.89 (5s, 15H, 5OAc). Anal. Calcd for $C_{22}H_{26}O_{12}N_2$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.76; H, 5.16; N, 5.49.

3.8. *N*-Acetyl, *N*-*p*-nitrophenyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (6)

This compound was prepared according to the general procedure. White crystals, yield, 97%; mp 161.5–162.5 °C; $[\alpha]_D^{20}$ +96.5 ($CHCl_3$), lit.[19] mp 159–160 °C; $[\alpha]_D$ +125 (EtOH), lit.[21] mp 161 °C; $[\alpha]_D$ +100 ($CHCl_3$).

3.9. Physical measurements

The X-ray diffraction measurements of compounds (**1**)–(**6**) were performed on a KUMA CCD κ-axis diffractometer with graphite-monochromated MoKα radiation (0.71073 Å) at 100 ± 2 K. The crystals were positioned at 62.3 mm from the KM4CCD camera. 856 frames were measured at 0.7° intervals with a counting time of 40 s, 664 frames were measured at 0.9° intervals with a counting time of 40 s, 748 frames were measured at 0.8° intervals with a counting time of 35 s, 856 frames were measured at 0.7° intervals with a counting time of 35 s, 748 frames were measured at 0.8° intervals with a counting time of 30 s, 748 frames were measured at 0.8° intervals with a counting time of 25 s, respectively, for (**1**)–(**6**). The data were corrected for Lorentz and polarization effects. The numerical absorption correction was not applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław, Poland) programmes.[22] The structures were solved by direct methods[23] and refined using SHELXL.[24] The refinement was based on F^2 for all reflections except for those with very negative F^2. The weighted R factor, wR and all goodness-of-fit S values are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions, which were refined while they participated in the hydrogen bonds. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2.[25]

The ^{13}C and ^1H spectra for $CDCl_3$ solutions were recorded on a UNITY-500 spectrometer, the 2D experiments were run using standard Varian software. Cross-polarization magic angle spinning solid-state ^{13}C NMR spectra were recorded at 100.1 MHz on a Bruker DRX-400 MHz spectrometer. Powder samples were spun at 8 kHz in 4 mm ZrO_2 rotor; contact time of 4–5 ms, repetition time of 8 s and spectral width of 25 kHz were used for accumulation of 200–500 scans. Chemical shifts were calibrated indirectly through the glycine CO signal recorded at 176.0 ppm, relative to TMS.

4. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from The Directory, Cambridge Crystallographic Data Centre, 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). Deposition numbers CCDC 297581 (**1**) 297582 (**2**) 297583 (**3**) 297584 (**4**) 297585 (**5**) and 297586 (**6**).

Acknowledgements

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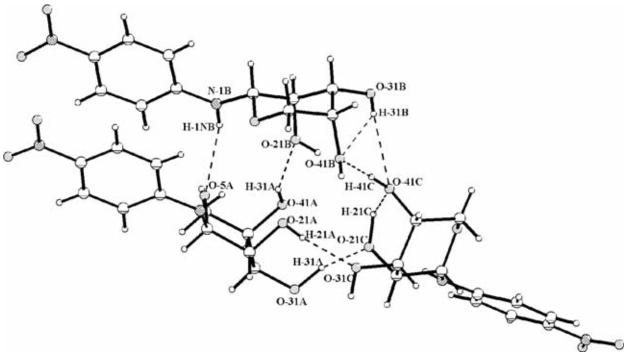

Correct **Figure 3**: Intermolecular interactions in the crystal lattice for *N*-*p*-nitrophenyl-α-D-ribopyranosylamine (**1**)).

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