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### Crystal Structure and Solid State $^{13}\text{C}$ Nmr Analysis of Methyl 3,4,6-Tri-*O*-Acetyl-2-Deoxy-2-(3-Phenylureido)- $\beta$ -D-Glucopyranoside

Romana Anulewicz; Iwona Wawer; Boguslawa Piekarska-Bartoszewicz; Andrzej Temeriusz

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**CRYSTAL STRUCTURE AND SOLID STATE  $^{13}\text{C}$  NMR ANALYSIS OF  
METHYL 3,4,6-TRI-*O*-ACETYL-2-DEOXY-2-(3-PHENYLUREIDO)- $\beta$ -D-  
GLUCOPYRANOSIDE**

Romana Anulewicz,<sup>a</sup> Iwona Wawer,<sup>b</sup> Bogusława Piekarska-Bartoszewicz<sup>a</sup> and  
Andrzej Temeriusz<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Warsaw University, Pasteura 1, Warszawa 02-093, Poland

<sup>b</sup>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 methyl 3,4,6-tri-*O*-acetyl-2-deoxy-(3-phenylureido)- $\beta$ -D-glucopyranoside was performed and showed that the molecules are associated by two  $\text{NH}\cdots\text{O}=\text{C}$  hydrogen bonds. One molecule with disorder of an acetyl group at C-4 was found in the asymmetric crystal unit. The signals in  $^{13}\text{C}$  CPMAS NMR spectrum are duplicated indicating that local symmetry is lower than those of the crystal.

**INTRODUCTION**

The series of substituted ureido sugars, the derivatives of methyl 2-amino-2-deoxy- $\beta$ -D-glucopyranoside and alkyl amines,<sup>1</sup> aryl amines,<sup>2</sup> amino acids,<sup>3</sup> and dipeptides<sup>4</sup> have

been recently synthesized and studied by means of NMR spectroscopy in solution and in the solid state. The aim of these investigations was to collect data on ureido sugars which are starting materials for the synthesis of nitrosoureas as antitumor agents.<sup>5</sup>

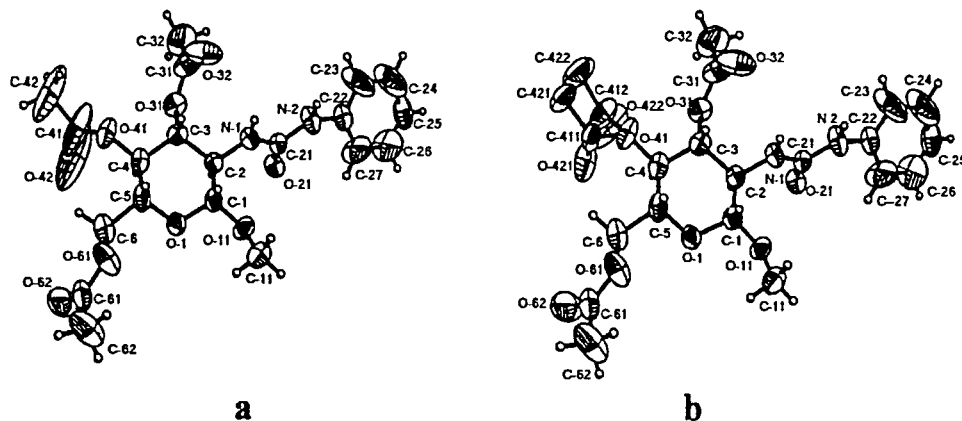
More valuable structural information can be obtained with a combined approach by X-ray diffraction analysis (XRD) and solid state NMR. One of the first such studies was that of lactulose.<sup>6</sup> Solid state NMR spectral data indicated the presence of three isomers: the  $\beta$ -furanose,  $\alpha$ -furanose and  $\beta$ -pyranose in a ratio 0.75 : 0.10 : 0.15. Another example of cocrystallization of  $\alpha$  and  $\beta$  anomers was that of D-glucosamine, as evidenced by XRD.<sup>7</sup>

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-[3-(2-phenylethyl)-ureido]- $\beta$ -D-glucopyranoside<sup>8</sup> and methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy- $\beta$ -D-glucopyranoside-*N*-carbamoyl-D-valine ethyl ester<sup>9</sup> were studied by us recently by means of XRD and solid state NMR. The method of synthesis yielded pure  $\beta$ -anomers.

## RESULTS AND DISCUSSION

*X-ray diffraction.*- The resulting SHELXL93<sup>10</sup> view of the methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside and the numbering of atoms are given in Fig. 1. The crystal data and structure refinement parameters are collected in Table 1 and the bond lengths, bond angles and selected torsion angles are presented in Tables 2, 3 and 4. An important aspect is the static and/or dynamic disorder within sugar moieties and aromatic rings. Thermal ellipsoids, drawn at 50% probability are large, like in other peracetylated ureido sugars, however, especially large are those for C=O atoms of the acetyl group at C-4 (Fig. 1a). Therefore, the structure was refined assuming structural disorder at C-41, O-42 and C-42 (Fig. 1b) and the occupations of both sites were 0.5. Some disorder was also obtained for aromatic carbons. The phenyl ring was refined assuming constant bond lengths of 1.39 Å. The XRD structure was solved with high accuracy for one molecule in the crystal unit although its structural fragments exhibit disorder, the quality of solution involving two independent molecules in the crystal unit is worse.

The  $\beta$ -D-glucopyranose ring exists in a  ${}^4C_1$  chair conformation. The deviation of C-1 and C-4 from the plane defined by C-2, C-3, C-5 and O-1 are -0.679(5) and



**Figure 1.** Molecular structure and atom numbering of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside. **a)** Thermal ellipsoids, drawn at 50% probability are large especially for C=O atoms of acetyl group at C-4, **b)** The structure is refined assuming structural disorder at C-41, O-42 and C-42.

0.684(6) Å, respectively. All acetyl groups are almost planar, like in numerous peracetylated pyranose derivatives. The conformation about the C-5–C-6 bond is nearly *gauche-trans* (*gt*) and the torsion angle C-4–C-5–C-6–O-61 =  $-169.9^\circ$ .

The urea moiety NH-CO-NH is planar and adopts an *anti Z,Z* conformation. The main plane of the urea moiety makes an angle of  $137.9(6)^\circ$  with the aromatic ring. In the crystal the molecules are associated by an intermolecular hydrogen bonding network in which each molecule participates in two NH $\cdots$ O hydrogen bonds with the same carbonyl oxygen. The distances of N-1 $\cdots$ O [3.061(5) Å] and N-2 $\cdots$ O [2.989(5) Å] are not equal. This hydrogen bonding pattern is frequently met in the crystals of substituted ureas, although in the previously studied ureido sugars<sup>8,9</sup> two different types of H-bonds were found: N-1–H $\cdots$ O=C (ureido carbonyl) and N-2–H $\cdots$ O (anomeric oxygen). According to the Cambridge Structural Database and to our knowledge there are four structures of ureido sugar determined by XRD. The same methyl 3,4,6-tri-*O*-acetyl-2-deoxy- $\beta$ -D-glucopyranoside moiety linked to N-1 was present in these compounds and various substituents at N-2: 2-phenylethyl (**1**),<sup>8</sup> D-valine (**2**),<sup>9</sup> dicyclohexyl (**3**),<sup>11</sup> and phenyl (**4**) (this work). In the crystal lattices of **1**–**3** sugar moieties are located on the left and right side of NH $\cdots$ O hydrogen bonded chains. The characteristic feature of the crystal structure

**Table 1.** Crystal data and structure refinement for methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside

Molecular formula	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>9</sub>
Molecular weight	438.43
Melting point (K)	467-471
[ $\alpha$ ] <sub>D</sub> <sup>20</sup> (°, <i>c</i> 1, chloroform)	+12.9
Temperature (K)	293(2) K
Wavelength (Å)	1.54178
Crystal system	orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions Å	
a	4.777(1)
b	16.726(2)
c	27.435(4)
Volume (Å) <sup>3</sup>	2192.1(5)
Z (molecules/cell)	4
Density (calculated, Mg cm <sup>-3</sup> )	1.328
Absorption coefficient (mm <sup>-1</sup> )	0.894
<i>F</i> (000)	928
Crystal size (mm)	0.2 x 0.2 x 0.25
$\Theta$ range for data collection (°)	3.09 to 80.17
Index ranges data for collection (°)	0 < <i>h</i> < 5, 0 < <i>k</i> < 17, 0 < <i>l</i> < 28
Reflections collected / unique	2487/2459
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data ( restraints) parameters	2454 / 0 / 278
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.234
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0753, <i>wR</i> 2 = 0.2000
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0924, <i>wR</i> 2 = 0.2156
Extinction coefficient	0.0033(7)
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.425 and -0.261

of ureido sugar with phenyl ring at N-2 is the location of the sugar moiety above (and below) other sugar moieties whereas aromatic rings stack in a column forming a hydrophobic zone (Figs. 2 and 3), the distance between aromatic rings is 4.777 Å. Contacts of the C-H...O type are present in the crystal [the C...O distances between parent

**Table 2.** Selected bond lengths [Å] for methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)-β-D-glucopyranoside

Atoms		Atoms		Atoms	
O-1-C-1	1.423(5)	C-3-C-4	1.509(6)	C-61-O-62	1.177(11)
O-1-C-5	1.432(5)	O-31-C-31	1.324(9)	C-61-C-62	1.538(12)
O-11-C-1	1.380(5)	C-31-O-32	1.232(10)	N-1-C-21	1.356(5)
O-11-C-11	1.431(7)	C-31-C-32	1.492(10)	C-21-O-21	1.214(6)
C-1-C-2	1.514(6)	C-4-O-41	1.434(5)	C-21-N-2	1.362(6)
C-2-N-1	1.439(5)	C-4-C-5	1.523(7)	N-2-C-22	1.416(4)
C-2-C-3	1.527(5)	C-5-C-6	1.528(7)	O-61-C-61	1.326(8)
C-3-O-31	1.425(6)	C-6-O-61	1.417(7)		

molecules are 3.380(6) Å], the interaction involves CH<sub>3</sub> hydrogens and the carbonyl oxygen from the acetyl group at C-3.

The structural disorder has further consequences, best seen by means of solid-state NMR.

*Solid state NMR.* The spectrum of solid methyl 3,4,6-tri-*O*-acetyl-2-deoxy-(3-phenylureido)-β-D-glucopyranoside recorded with cross polarization and magic angle spinning techniques (CPMAS) at 75.5 MHz is illustrated in Fig. 4. Chemical shifts from solid phase and CDCl<sub>3</sub> solution spectra are collected in Table 5. Inspection of the solid state spectrum shows splitting of the resonances, best seen for sugar carbons. The NMR spectrum was recorded prior to the XRD study. Since crystallography showed only one molecule in the asymmetric crystal unit, the NMR measurements were repeated after recrystallization of the compound. Another single crystal was studied by XRD, but the results from both methods did not change.

The signals from carbon atoms linked to nitrogen (C-2, N-CO-N) are broader due to residual <sup>13</sup>C-<sup>14</sup>N (quadrupolar) interaction. The chemical shift of the ureido carbonyl carbon is 155.9 ppm in solution and 156.6 ppm in the solid state, thus only a small downfield shift is observed as a result of the formation of a hydrogen bond.

Comparison of the solid-state and solution chemical shifts enables detection of rigid and flexible structural fragments, the latter exhibiting larger shielding changes. For

**Table 3.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside [ $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_j$  tensor].

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O-1	9255(9)	6349(2)	546(1)	48(1)
O-11	9389(10)	6309(2)	-278(1)	54(1)
C-1	8056(12)	5990(3)	124(1)	41(1)
C-11	8230(2)	7051(3)	-439(2)	67(2)
C-2	8510(9)	5094(2)	130(1)	37(1)
C-3	7290(11)	4758(2)	602(1)	41(1)
O-31	8021(10)	3937(2)	656(1)	54(1)
C-31	6114(19)	3394(3)	543(2)	66(2)
O-32	3821(15)	3557(3)	363(2)	96(2)
C-32	7170(3)	2566(4)	626(3)	110(4)
C-4	8411(11)	5196(3)	1042(1)	45(1)
O-41	6959(11)	4895(2)	1461(1)	62(1)
C-5	7903(12)	6089(3)	984(1)	46(1)
C-6	9160(17)	6592(3)	1394(2)	62(2)
O-61	8096(12)	7378(3)	1343(2)	75(1)
C-61	9412(19)	7956(4)	1581(2)	70(2)
O-62	11391(19)	7838(3)	1826(2)	104(2)
C-62	8040(3)	8776(5)	1495(4)	119(4)
N-1	7263(9)	4719(3)	-289(1)	40(1)
C-21	8781(10)	4469(2)	-678(1)	34(1)
O-21	11315(8)	4510(2)	-696(1)	44(1)
N-2	7141(11)	4169(4)	-1040(2)	59(1)
C-22	8125	3851	-1487	48
C-23	6859	3168	-1673	179
C-24	7693	2864	-2121	176
C-25	9795	3244	-2384	83
C-26	11061	3928	-2199	142
C-27	10227	4231	-1750	119

rigid systems such as the chair-like ring of  $\beta$ -D-glucopyranose, only the  $\text{OCH}_3$  group at the anomeric carbon and  $\text{OCH}_2$  group at C-5 undergo reorientation. The differences in chemical shifts  $\Delta = \delta_{\text{liquid}} - \delta_{\text{solid}}$  are significant for C-1,  $\text{OCH}_3$  and C-6, for these carbons, deshielding of 1.9 to 4.0 ppm occurs in the solid state (Table 5). The chemical shifts of acetyl group carbons are almost the same as those in solution.

**Table 4.** Selected bond angles ( $^{\circ}$ ) for methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside

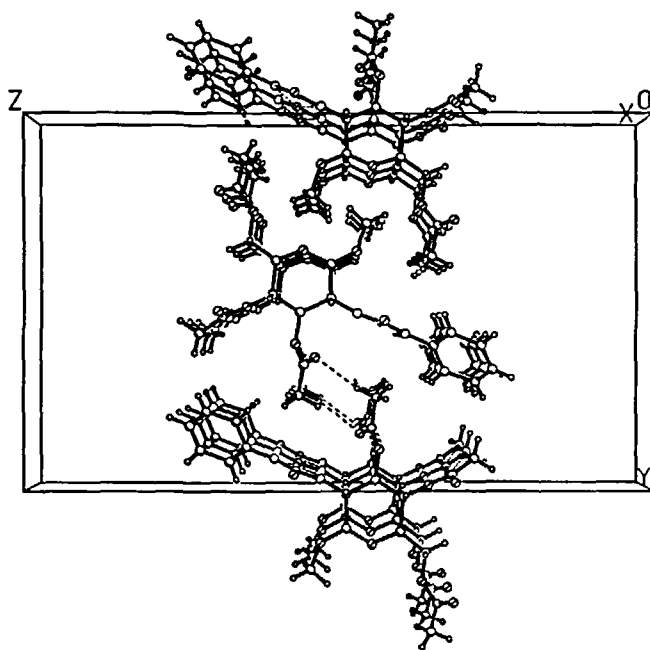
Atoms		Atoms	
C-1-O-1-C-5	111.9(4)	O-41-C-4-C-3	107.5(4)
C-1-O-11-C-11	113.8(5)	O-41-C-4-C-5	110.5(4)
O-11-C-1-O-1	107.5(4)	C-3-C-4-C-5	109.6(4)
O-11-C-1-C-2	108.9(3)	O-1-C-5-C-4	108.3(4)
O-1-C-1-C-2	110.6(4)	O-1-C-5-C-6	105.9(4)
N-1-C-2-C-1	111.4(4)	C-4-C-5-C-6	113.6(4)
N-1-C-2-C-3	111.0(4)	O-61-C-6-C-5	107.3(5)
C-1-C-2-C-3	108.6(3)	C-61-O-61-C-6	117.3(5)
O-31-C-3-C-4	107.2(4)	O-62-C-61-O-61	122.6(7)
O-31-C-3-C-2	110.5(4)	O-62-C-61-C-62	125.4(7)
C-4-C-3-C-2	111.4(4)	O-61-C-61-C-62	111.9(7)
C-31-O-31-C-3	117.9(5)	C-21-N-1-C-2	122.8(4)
O-32-C-31-O-31	123.7(5)	O-21-C-21-N-1	123.2(4)
O-32-C-31-C-32	124.6(9)	O-21-C-21-N-2	124.4(4)
O-31-C-31-C-32	111.6(9)	N-1-C-21-N-2	112.4(4)

Proton spin-lattice relaxation times  $T_1$ ,  $T_{1\rho}$  and proton second moment have been measured for polycrystalline methyl  $\beta$ -D-pyranosides.<sup>12</sup> Two reductions of the second moment were observed, from C-3 reorientation of  $\text{OCH}_3$  groups (minima at low temperatures, below  $70^{\circ}\text{K}$ ) and *trans-gauche* conformational motion of  $\text{CH}_2\text{OH}$  group – slightly below room temperature. Large thermal ellipsoids (Fig. 1) and significant shielding differences  $\Delta = \delta_{\text{liquid}} - \delta_{\text{solid}}$  are in agreement with the above findings indicating that also in the crystal of the studied ureido sugar the movement of methyl groups takes place.

The resonances of sugar carbons (and of one acetyl group) are split and the separation is 0.7-1.9 ppm. Various locations of the acetyl substituent at C-4 results in non-equivalence of 0.4 ppm for carbonyl carbons.

*General remarks on the structure of ureido sugars.* Some geometrical parameters of the four studied ureido sugars and the types of hydrogen bonds are collected in Table 6.

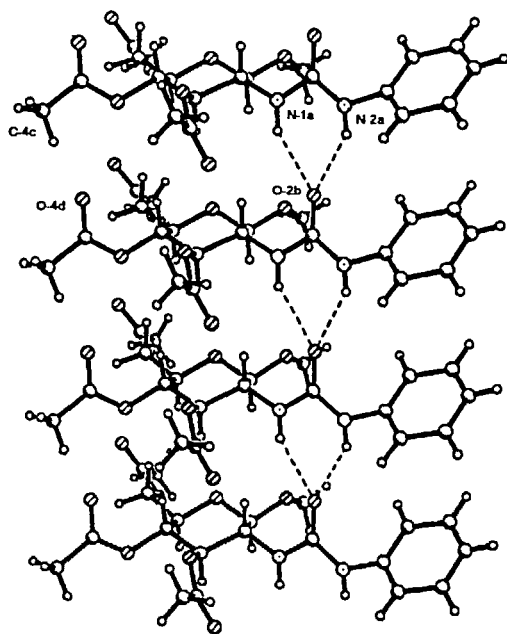




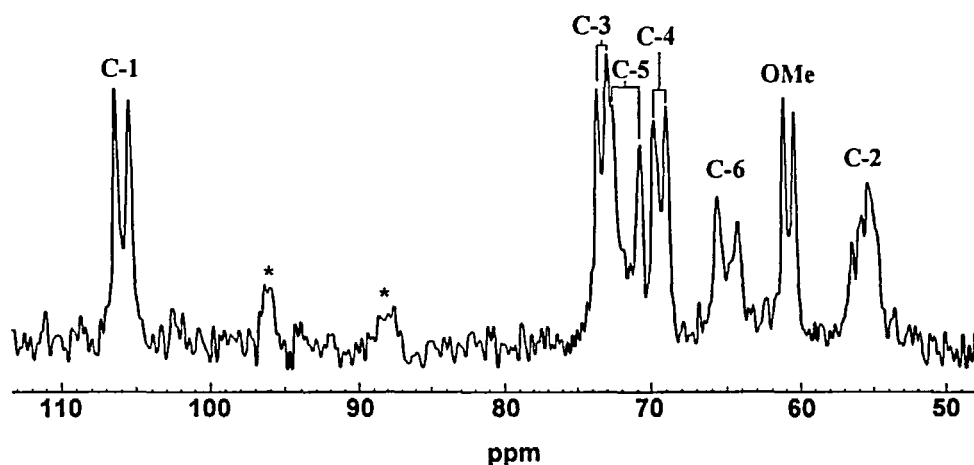
**Figure 2.** The crystal structure of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside. The intermolecular CH $\cdots$ O contacts are indicated by broken lines.

It seemed interesting to compare the C-N and C=O bond lengths with their optimal values<sup>13</sup> of 1.334 and 1.265 Å, respectively, since the deviations from optimal values may be a measure of delocalization of  $\pi$ -electrons over the molecular fragment. In all four compounds the N-1-CO and N-2-CO bonds are longer than the optimal C-N bond and the C=O bonds are shorter than the optimal value. The lengths of C=O bonds are close to that of typical double bonds (1.241 Å). The longest C=O bond could be expected for **4** due to the two hydrogen bonds formed, however, this bond is the shortest (additional interaction with the  $\pi$ -electrons of the phenyl ring which could influence the delocalization within the urea fragment is less important due to the twisting of the ring). The N-1-CO and N-2-CO bonds in **2**, **3**, **4** are longer than typical CN bond in ureas (1.347 Å).<sup>14</sup>

One should take into account that the XRD pattern is an average and reflects mainly the lattice periodicity. XRD may not be sensitive enough to detect that the symmetry of the sugar moiety is lower than that of the whole lattice. It can be concluded



**Figure 3.** The crystal structure of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside. The intermolecular NH $\cdots$ O hydrogen bonds are indicated by broken lines.



**Figure 4.** The  $^{13}\text{C}$  NMR CPMAS spectrum of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenylureido)- $\beta$ -D-glucopyranoside in the range of the sugar carbons (\* side bands).

**Table 5.**  $^{13}\text{C}$  NMR chemical shifts for methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(3-phenyl-ureido)- $\beta$ -D-glucopyranoside (ppm, TMS). The signals of aromatic carbon atoms are neglected.

	C-1	C-2	C-3	C-4	C-5	C-6	OCH <sub>3</sub>	NCON	CH <sub>3</sub>	Acetyl
In CDCl <sub>3</sub>	103.0	55.4	72.9	69.0	71.7	62.3	57.0	155.9	20.5 20.6 20.7	169.4 170.6 170.9
Solid	106.2	56.0	73.5	69.6	72.5	65.5	61.0	156.6	19.6	170.1
	105.3	55.1	72.8	68.8	70.6	64.2	60.3	(broad)	20.5	170.5 171.2; 170.8
Splitting (solid)	0.9	0.9	0.7	0.8	1.9	1.3	0.7			0.4
$\Delta$	-3.2	-0.6	-0.6	-0.6	-0.8	-3.2	-4.0	-0.7	0.6	-0.6
	-2.3	+0.3	+0.1	+0.2	+1.1	-1.9	-3.3		0.1	+0.1
									0.2	-0.3/+0.1

**Table 6.** The comparison of selected XRD results for ureido sugars

	Substituents at N-2			
	Phenylethyl (1)	D-valine (2)	Dicyclohexyl (3)	Phenyl (4)
Bond length, Å				
C-2-N-1	1.443(5)	1.423(7)	1.445(8)	1.446(5)
N-1-CO	1.348(5)	1.376(7)	1.354(9)	1.362(4)
C=O	1.250(5)	1.221(7)	1.229(9)	1.215(5)
CO-N-2	1.342(5)	1.351(8)	1.367(8)	1.361(5)
N-2-C			1.458(8) ( <i>Z</i> ) 1.471(9) ( <i>E</i> )	1.417(5)
Bond angle, (°)				
N-1-CO-N-2	115.5(3')	113.8(5')	116.5(6')	111.9(3')
H-bonding, Å				
N-1-H...OC(acetyl)			3.160(9)	
N-1-H...OC(ureido)	2.902(7)	2.927(6)		3.061(5)
N-2-H...OC(ureido)				2.989(5)
N-2-H...O(anomeric)	2.904(5)	3.063(7)		

that in some situations involving lattice and site symmetry effects, high-resolution solid state NMR analysis is more sensitive to local symmetry than X-ray diffraction analysis.

## EXPERIMENTAL

Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-(3-phenylureido)- $\beta$ -D-glucopyranoside (**4**) was synthesized according to the described procedure.<sup>2</sup> Single crystal was obtained by recrystallization from ethanol.

The X-ray measurements of the crystal were made on KM-4 diffractometer with graphite monochromated CuK $\alpha$  radiation. The data were collected at room temperature using the  $\omega$ -2 $\theta$  scan technique. The intensity of control reflections for the compound varied by less than 5% and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects but no absorption correction was applied. The structure was solved by direct methods<sup>15</sup> and refined using SHELXL.<sup>10</sup> Non-hydrogen atoms were refined anisotropically, whereas H-atoms were placed in calculated positions and their thermal parameters were refined isotropically, in the last cycles they were refined with isotropic displacement parameters. Atomic scattering factors were taken from the International Tables.<sup>16, 17</sup>

<sup>13</sup>C NMR spectra were recorded on a Bruker MSL-300 instrument at 75.5 MHz for CDCl<sub>3</sub> solution and the solid state. Cross polarization magic angle spinning (CP MAS) solid state spectra were recorded with spinning speed of 3.4 and 10 kHz, and a contact time of 4 ms. A repetition time of 6 s and a spectral width of 20 kHz were used for accumulation of 400 scans. Chemical shifts were calibrated indirectly through the glycine C=O signal recorded at 176.3 ppm relative to TMS.

## ACKNOWLEDGMENTS

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