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Crystal structure and solid state ^{13}C NMR analysis of *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide derivative of *p*-chloroaniline, *N*,*N*-diethylamine, *N*-methylaniline and *N*-ethylaniline

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Abstract

The X-ray diffraction analysis of *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′-*p*-chlorophenyloxamide (**1**), *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′,*N*′-diethyloxamide (**2**), *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl), *N*′-methyl, *N*′-phenyloxamide (**3**), *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl), *N*′-ethyl, *N*′-phenyloxamide (**4**) was performed. It was found that the oxamide group in compounds **1**–**4** can be characterized as two structurally independent amides because there is no π conjugation across the oxalyl OC–CO bond. Only the oxamide group of **1** is planar and adopts trans conformation stabilized as two intramolecular N–H···O hydrogen bonds.

Keywords: Crystal structure; ^{13}C NMR analysis; X-ray diffraction analysis

1. Introduction

Oxamides are important as ligands in organometallic complexes.[1] Many oxamides show biological activity as pesticides,[2] plant growth regulators,[3] cephalosporin bactericides,[4] and HIV-1 protease inhibitors.[5] In an earlier report,[6] we have described the synthesis of several new oxamides, derivatives of D-glucosamine and different amines. Owing to various functional groups, several conformations could be expected, as well as intramolecular hydrogen bonding. It is therefore necessary to study in more detail the structure of the new oxamides. In this report, we present the results of the X-ray diffraction analysis of compounds **1**–**4** (Scheme 1), supported by ^{13}C CP MAS NMR spectroscopy.

2. Results and discussion

The oxamide derivatives were prepared by the reaction of oxalyl chloride with methyl

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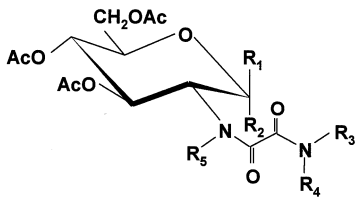
2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α, and β-D-glucopyranoside and then with the corresponding mono- (*p*-chloroaniline **1**) or diamine (*N*,*N*-diethylamine **2**, *N*-methylaniline **3**, *N*-ethylaniline **4**). The details of the synthesis of oxamide sugars have been reported previously.[6]

Suitable crystals of **1**–**4** were obtained by slow crystallization from ethanol. The configuration, conformation and atom numbering are shown in Fig. 1. Crystal data and structural refinement are specified in Table 1. Selected bond lengths, bond angles and major torsion angles for **1**–**4** are given in Tables 2–4. The inspection of Fig. 1 shows that only compound **1** has two NH groups which could be involved in hydrogen bonding, one hydrogen bond donor exists in **2**, whereas neither **3** nor **4** can form intra- or intermolecular hydrogen bonds.

The oxamide part of molecule **1** adopts planar trans conformation and torsion angle N-1–C-21–C-22–N-2 is 179.0° (Fig. 2). This conformation is stabilized by two intramolecular hydrogen bonds N–H···O completing the five-membered rings H-7–N-1–C-21–C-22–O-22 and H-8–N-2–C-22–C-21–O-21. The H-7···O-22 distance is 2.303(4) Å and the H-8···O-21 distance is 2.232(4) Å. The sugar part of the molecule is located in *Z* position to oxamide residue (H-2 and H-7 are in anti position) and adopts an *ac* (anticlinal) conformation with respect to C-1 and C-3 (the torsion angle C-1–C-2–N-1–C-21 = 138.6°). In compound **1** besides the planar oxamide unit, also the phenyl ring is only slightly twisted



1 R_1= H, R_2= OMe, R_3 = H, R_4 = *p*ClPh, R_5 = H

2 R_1= H, R_2= OMe, R_3 = Et, R_4 = Et, R_5 = H

3 R_1= OMe, R_2= H, R_3= Me, R_4 = Ph, R_5 = OAc

4 R_1= OMe, R_2= H, R_3= Et, R_4 = Ph, R_5 = OAc

Scheme 1.

and occupies almost the same plane (C-22–N-2–C-23–C-24 = 16.7°). In the crystal, the molecules of **1** are associated by intermolecular hydrogen bonds formed by N-1–H with acetyl oxygen C-3–OAc (O-32) of parent molecule. Sugar units are located on the right and, a row below, on the left side of the hydrogen bonded chain (Fig. 3). The phenyl ring of one molecule is perpendicular to that in the adjacent molecule.

The oxamide group of compound **2** is not planar, atoms N-1–C-21 are strongly twisted with respect to C-22–N-2 and an *ac* conformation with a torsion angle N-1–C-21–C-22–N-2 = 98.1° is favored (Fig. 2). It is evident that one intramolecular hydrogen bond H-7–O-22 [2.026(4) Å] is not enough to stabilize the trans conformation. The sugar part of the molecule, similarly to compound **1,** is present in *Z* position with respect to oxamide residue (H-2 and H-7 are in anti position) and the oxamide group accepts an *ac* conformation with respect to C-1 and C-3 (the torsion angle C-1–C-2–N-1–C-21 = 93.4°). The atoms of carbonyl group C-22, O-22, and the atoms N-2, C-23, C-25 of diethylamine group of the molecule of **2** are located within one plane and the torsion angle O-22–C-22–N-2–C-23 = 0.4° (O-22–N-2–C-23–C-25 = −179.2°). The two planes are almost perpendicular.

Compounds **3** and **4** show (see the respective torsion angles 93.4 and 98° in Table 4) slightly different conformations in comparison with compounds **1** and **2**. The oxamido part of molecules **3** and **4** adopts an *ac* conformation and the torsion angle N-1–C-21–C-22–N-2 is 107.0 and 108.2°, respectively. Due to the presence of acetyl residue at N-1, the sugar part (in contrast to compound **1** and **2**) is present in *E* position with respect to the oxamide residue. Oxamide groups adopt a skew conformation with respect to C-1 and C-3 (the torsion angle C-1–C-2–N-1–C-22 = 61.4 and 61.5° in **3** and **4**, respectively). The atoms of carbonyl group C-22, O-22, and the atoms N-2, C-23 and C-25 of methylaniline group of the molecule **3**, or of ethylaniline group of the molecule **4** form a plane and the torsion angle O-22–C-22–N-2–C-23 = 175.2 and 175.8°, respectively. The phenyl ring is turned by 58.6°

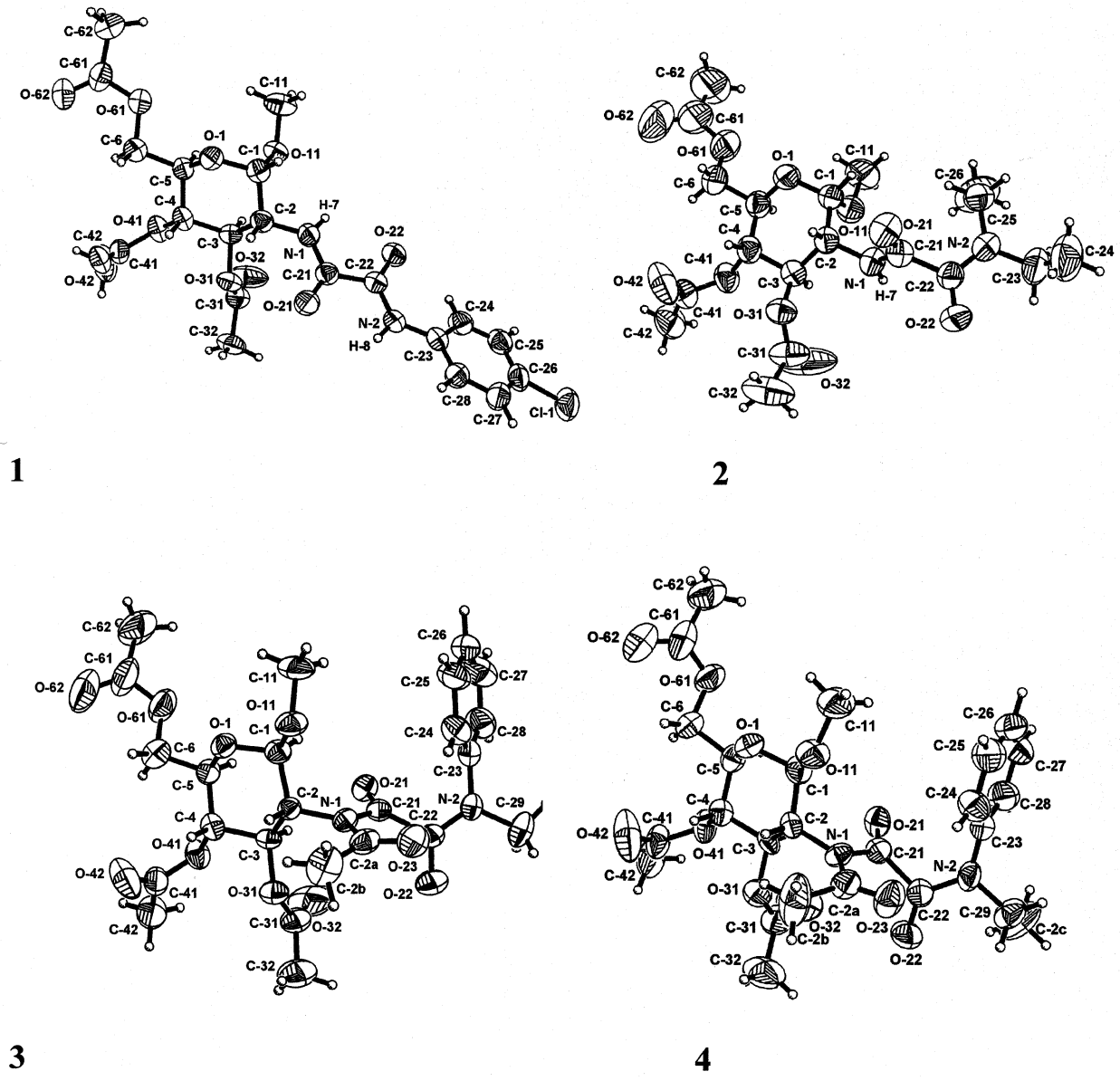


Fig. 1. Molecular structure and atomic numbering of **1**: *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′-*p*-chlorophenyloxamide; **2**: *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′,*N*′-dietyloxamide; **3**: *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl), *N*′-methyl, *N*′-phenyloxamide; **4**: *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl), *N*′-ethyl, *N*′-phenyloxamide (**4**).

(**3**) and 63.2° (**4**) of the plane of atoms C-22, N-2, C-21.

The C=O (1.169–1.219 Å) and C–N (1.299–1.372 Å) bonds of the oxamide group of compounds **1**–**4** display a double-bond character whereas the OC–CO bonds (1.494–1.537 Å) are slightly longer than typical single bonds,[7] which suggests electronic delocalization within the O=C–N groups.

The *Z*/*E* isomerism in substituted oxamides has been previously studied.[8,9] Alkyl- or aryloxamides may exist in two conformations, cis or trans, the planar trans location of the dicarbonylic function is possible only when it is stabilized by an intramolecular hydrogen bond. For example, in *N*,*N*′-bis[(2-hydroxy)phenyl]oxamide, and for other similar oxamides the trans conformation was stabilized by two five-membered rings formed by the intramolecular hydrogen bond NH···O.[8] It has been found by molecular mechanics calculations that for *N*,*N*′-bis[(2-hydroxy)phenyl]-

Table 1
Crystal data and structure refinement for *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide **1–4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{21}H_{25}ClN_2O_{10}$	$C_{19}H_{30}N_2O_{10}$	$C_{24}H_{30}N_2O_{11}$	$C_{25}H_{32}N_2O_{11}$
Formula weight	500.88	446.45	522.50	536.53
Melting point (K)	478–480	406–409	459–460	449–452
$[\alpha]_D^{20}$ (°, *c* 1, chloroform)	+65.1	+76.3	−35.7	−42.3
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_1$
Unit cell dimensions				
a (Å)	10.174(2)	9.547(2)	9.432(2)	9.507(2)
b (Å)	7.2440(1)	14.797(3)	8.302(2)	8.650(2)
c (Å)	16.107(3)	16.842(3)	16.418(3)	16.248(3)
β (°)	105.25(3)		99.50(3)	98.22(3)
V (Å)3	1145.3(3)	2379.1(8)	1268.0(5)	1322.4(5)
Z (molecules/cell)	2	4	2	2
D_{calcd} (Mg/cm)	1.452	1.246	1.369	1.347
Absorption coefficient (mm^{-1})	0.227	0.101	0.109	0.106
F(000)	524	945	552	568
Crystal size (mm)	0.4 × 0.35 × 0.3	0.4 × 0.3 × 0.32	0.4 × 0.3 × 0.3	0.38 × 0.35 × 0.3
θ range for data collection (°)	2.07–29.93	3.46–28.67	2.19–23.45	2.16–26.42
Index ranges data for collection (°)	$-12 \le h \le 12$, $0 \le k \le 10$, $-17 \le l \le 0$	$-12 \le h \le 6$, $-19 \le k \le 19$, $-22 \le l \le 21$	$0 \le h \le 10$, $0 \le k \le 8$, $-17 \le l \le 16$	$-11 \le h \le 11$, $0 \le k \le 9$, $-16 \le l \le 16$
Reflections collected	2427	14248	1891	4356
Independent reflections	2372 [$R_{int} = 0.0532$]	5212 [$R_{int} = 0.0215$]	1776 [$R_{int} = 0.0476$]	2490 [$R_{int} = 0.0156$]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data (restraints) parameters	2372/1/332	5212/0/311	1776/1/365	2490/1/375
Goodness-of-fit on F^2	1.058	1.190	1.016	1.008
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0627$, $wR_2 = 0.1509$	$R_1 = 0.0890$, $wR_2 = 0.2859$	$R_1 = 0.0430$, $wR_2 = 0.0982$	$R_1 = 0.0653$, $wR_2 = 0.1642$
R indices (all data)	$R_1 = 0.0902$, $wR_2 = 0.1852$	$R_1 = 0.1064$, $wR_2 = 0.3134$	$R_1 = 0.0863$, $wR_2 = 0.1194$	$R_1 = 0.1658$, $wR_2 = 0.2485$
Largest difference peak and hole (e/Å^3)	0.322 and −0.614	0.462 and −0.301	0.171 and −0.190	0.442 and −0.416

oxamide the trans conformer is more stable by 9.96 kcal/mol than the cis conformer.[10]

The substituted oxamides show a significant torsional angle (of about 90°) around the central OC–CO bond, which is unusually long. The twisting results from the likely charged oxygen, carbon and nitrogen repulsions.

On the other hand, for tetrasubstituted oxamides {in 2-[2-[methyl(phenyl)amino-1,2-dioxoethyl] - 1,2,3,4 - tetrahydroisoquinoline} four conformers (*Z*-trans-*Z*, *Z*-trans-*E*, *E*-trans-*Z* and *E*-trans-*E*), were assigned by NMR measurements.[9] The authors identified the signals as being due to two major and two minor conformers. For this compound, the barrier to rotation around the N–$C_{aromatic}$ or N–C_{cyclic} bond was low enough to observe four isomers simultaneously. All isomers showed the same trans conformation about the N–C=O bond which was supported by the NOE data. We found trans conformation only in compound **1**.

^{13}C CP MAS.—Solid state NMR spectroscopy combined with X-ray diffraction can be considered as complementary tools to establish the molecular structure of organic

Table 2
Selected bond lengths (Å) for *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide **1–4**

Atoms	Compound			
	1	**2**	**3**	**4**
C-2–N-1	1.429(6)	1.442(4)	1.448(7)	1.458(10)
N-1–C-21	1.307(7)	1.330(4)	1.372(8)	1.371(11)
C-21–O-21	1.215(6)	1.217(4)	1.193(8)	1.183(11)
C-21–C-22	1.494(7)	1.516(5)	1.500(9)	1.537(13)
C-22–O-22	1.220(6)	1.219(4)	1.213(6)	1.169(11)
C-22–N-2	1.299(6)	1.328(5)	1.299(7)	1.346(11)
C-2a–O-23			1.181(7)	1.170(10)
N-1–C-2a			1.388(8)	1.375(12)

Table 3
Selected bond angles (°) for *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide **1–4**

Atoms	Compound			
	1	**2**	**3**	**4**
C-21–N-1–C-2	122.3(4)	121.6(3)	118.3(5)	117.6(7)
C-21–N-1–C-2a			120.3(6)	120.6(8)
O-21–C-21–N-1	125.2(4)	123.4(3)	121.5(6)	123.0(8)
O-21–C-21–C-22	119.7(4)	121.2(3)	118.6(6)	119.7(8)
C-2a–N-1–C-2			121.4(5)	121.7(7)
N-1–C-21–C-22	115.1(4)	115.3(3)	118.9(6)	116.4(8)
N-1–C-2a–C-2b			118.5(7)	116.9(9)
O-22–C-22–N-2	125.5(4)	124.3(3)	125.0(5)	126.8(8)
O-23–C-2a–C-2b			121.8(6)	121.8(9)
O-22–C-22–C-21	119.9(4)	118.4(3)	116.6(5)	117.8(8)
N-2–C-22–C-21	114.5(4)	117.3(3)	117.7(5)	114.5(8)
C-22–N-2–C-23	128.4(4)	119.2(4)	122.0(4)	123.0(7)

compounds. Additionally, our interest was to gain some insight into the conformations of the oxamido and sugar units without the influence of any solvent. Therefore the ^{13}C chemical shifts were measured in the spectra of solids **1–4** recorded by cross-polarization magic angle spinning technique. The spinning speed of ca. 8 KHz was enough to circumvent side bands.

The ^{13}C CP MAS NMR spectra **2** and **3** are shown in Fig. 4. The majority of ^{13}C resonances could be assigned directly by comparison with the solution data.[6] The signals of acetyl group carbons are narrow and their chemical shifts are almost the same as these in $CDCl_3$ solutions (Table 5). The signals of carbons bonded to nitrogen [N–C(O)CH_3, N-1–CO, N-4–CO, N-1–C-2, N-4–C_{methyl}, N-4–C_{phenyl} and N-4–CH_2] are broader or/and splitted into asymmetric doublets due to the residual $^{13}C-^{14}N$ dipolar coupling.[11] These residual splittings or broadening make possible the assignment of carbons in the proximity of nitrogen.

In solution there is only one resonance for each set of chemically equivalent carbons because of rapid conformational averaging. In the solid state, distinct peaks may be observed for each type of carbon.[12] The amide carbon chemical shifts of oxamides with two intramolecular hydrogen bonds were within 156.9–159.0 ppm, i.e., appeared at higher field than the monoamides (168.3–169.1 ppm).[8] The chemical shift of NCO carbon of **1** equal to 157.4 ppm is in agreement with the above data. Somewhat unexpectedly, only one resonance (which appeared as a characteristic unequal doublet) was observed for both carbonyl carbons. This indicates that the nitrogen lone pair is delocalized over the π system of the adjacent carbonyl bond, and also that the state of the two carbonyl groups is similar. The lack of a significant high-frequency shift, as compared with the solution, indicates that the two intramolecular hydrogen bonds are present in both phases. As mentioned above, in the crystals of **1** the N-1–H group also forms an intramolecular hydrogen bond. The involvement in additional interaction results in a low-frequency shift of C=O of 2.7 ppm (cooperative effect).

Inspection of chemical shifts of C=O carbon confirms that one C=O group in compound **2** is involved in intermolecular hydrogen bonds (δ 167.4 ppm in the solid state, 161.5 in solution). Although such hydrogen bonds can exist in solution, yet in the solid state all C=O carbons are involved. Therefore a high-frequency shift ($\Delta = 5.9$ ppm) due to the formation of this bond is observed for C=O in the solid state spectra, as compared with those in solution. A smaller effect of $\Delta = 2.5$ ppm is observed for a second C=O group in **2**. The chemical shifts of C=O carbons in **3** and **4** are almost the same in both phases since in these

Table 4
Selected torsion angles (°) for *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide **1**–**4**

Atoms	Compound			
	1	**2**	**3**	**4**
C-1–C-2–N-1–C-21	138.6(5)	93.4(4)	−65.0(6)	−66.2(10)
C-3–C-2–N-1–C-21	−98.0(6)	−143.7(3)	61.4(6)	61.5(9)
C-1–C-2–N-1–C-2a			114.3(5)	108.9(10)
C-3–C-2–N-1–C-2a			−119.2(5)	−123.3(9)
C-21–N-1–C-2a–O-23			14.5(8)	13.3(2)
C-2–N-1–C-2a–O-23			−164.8(5)	−161.6(9)
C-2a–N-1–C-21–O-21			−170.5(5)	−167.2(9)
O-21–C-21–C-22–N-2	−0.2(8)	−84.2(5)	62.7(8)	61.8(12)
O-21–C-21–C-22–O-22	179.0(6)	95.1(5)	−108.2(7)	−108.5(11)
N-1–C-21–C-22–O-22	0.2(7)	−82.6(4)	62.0(8)	61.5(12)
N-1–C-21–C-22–N-2	−179.0(5)	98.1(4)	−127.0(6)	−128.2(9)
O-22–C-22–N-2–C-23	−1.9(9)	−0.4(6)	−175.2(7)	−179.8(11)
C-22–N-2–C-23–C-24	−16.7(9)	−92.7(7)	58.8(9)	63.2(13)

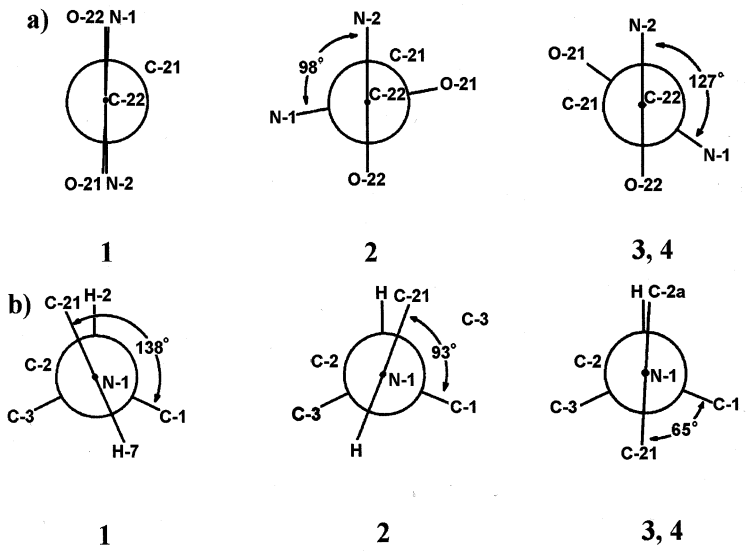


Fig. 2. Dihedral angels (a) N-1–C-21–C-22–N-2 and (b) C-1–C-2–N-1–C-21 of *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′-*p*-chlorophenyloxamide (**1**), *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′,*N*′-dietyloxamide (**2**), *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl), *N*′-methyl, *N*′-phenyloxamide (**3**), and *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl)-*N*′-ethyl, *N*′-phenyloxamide (**4**).

compounds intra- or intermolecular hydrogen bonds do not exist.

It seemed worth considering the chemical shifts of pyranose carbons in compound **1**–**4**. In the *N*-acetyl, *N*-(methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranosid-2-yl)-oxamides **3** and **4**, which do not form hydrogen bonds, a significant low-frequency shift ($\Delta = 3.0$, 3.1 ppm, respectively) of C-4 and a smaller shift ($\Delta = -1.4$, -1.1 ppm) in opposite direction of C-3 resonance were observed.

Different conformations, appear in solid *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-oxamides **1** and **2** in comparison with the solution. The chemical shift of anomeric carbon C-1 is larger by 1.5 ppm in both compounds, also that of methyl carbon of OMe group linked to C-1 is larger by 3.7 and 1.5 ppm in **1** and **2**, respectively. The deshielding of C-6 ($\Delta = -1.1$ and -1.5 ppm for **1** and **2**, respectively) can be noticed as well as of C-5 in **1** ($\Delta = -2.4$ ppm).

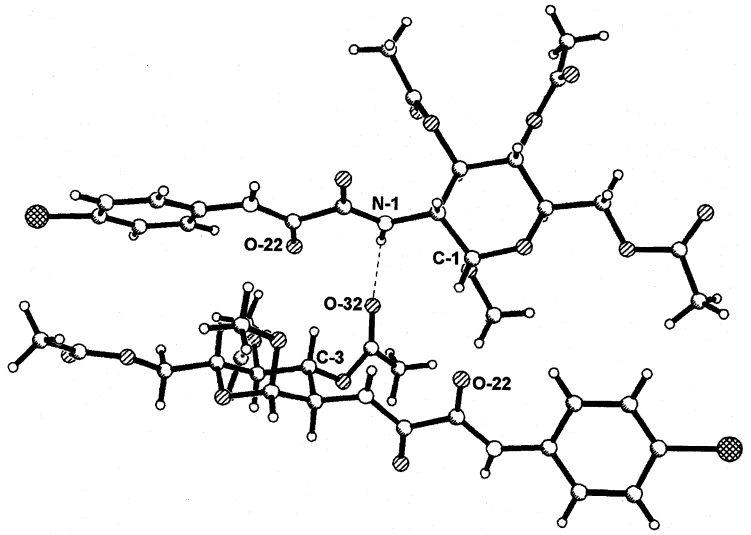


Fig. 3. Intermolecular hydrogen bond (broken line) of *N*-(methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosid-2-yl)-*N*′-*p*-chlorophenyloxamide (**1**).

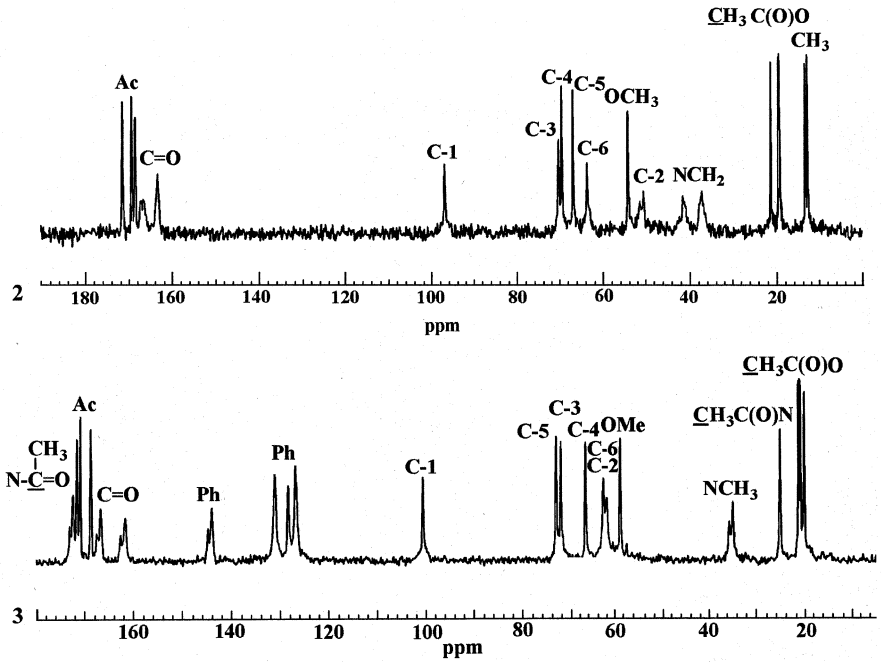


Fig. 4. ^{13}C CP MAS spectrum **2**: *N*-(methyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside-2-yl), *N*′,*N*′-di-ethyloxamide, and **3**: *N*-carbomethoxy, *N*-(methyl 3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside-2-yl), *N*′-methyl, *N*′-phenyloxamide.

3. Experimental

(Methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-*N*-oxamide derivative of *p*-chloroaniline (**1**), *N*,*N*-diethyloamine (**2**), *N*-methylaniline (**3**), and *N*-ethylaniline (**4**), was synthesized according to the described procedure.[6] Single crystals were obtained by recrystallization from EtOH.

X-ray measurements of the crystal **2** were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo K_α radiation. The crystal was positioned at 65 mm from the KM4CCD camera, 512 frames were measured at 1.0° intervals with a counting time of 10 s. The X-ray measurements of the compounds **1**, **3** and **4** were carried out on a KM-4 Kuma diffractometer

Table 5
^{13}C NMR data (δ in ppm,) for *N*-(methyl 3,4,6-tri-*O*-acetyl-α, and β-D-glucopyranosid-2-yl)-oxamide **1**–**4** in solid state and (in parentheses) the differences Δ (ppm) = $\delta_{liquid} - \delta_{solid}$ [a]

Atom	**1**	**2**	**3**	**4**
C-1	96.44 (1.5)	96.67 (1.5)	99.74	99.33
C-2	53.51	50.60 (1.0)	61.36	61.02
C-3	71.22	70.29	70.91 (−1.4)	70.63 (−1.1)
C-4	66.56 (1.7)	69.43 (−1.0)	65.83 (3.0)	65.71 (3.1)
C-5	70.09 (−2.4)	66.86	71.89	71.65
C-6	63.07 (−1.1)	63.54 (−1.5)	62.06	61.93
O–CH_3	51.91 (3.7)	54.02 (1.5)	58.54	57.90
C=O	157.44 (2.7)	167.4 (−5.9), 163.3 (−3.6)	166.6, 161.5	166.4, 161.0
CH_3CON			25.22 (−1.6)	24.27
CH_3COO	21.00, 20.82, 20.57	19.38, 19.12	21.38, 20.95, 20.20	20.59, 20.09, 19.04
CONR			172.8	172.2
COOR	172.0, 169.5	171.3, 169.2, 168.47	171.4, 170.7, 168.5	170.8, 170.4, 168.1
N–CH_2		41.63, 37.26		45.36
C–CH_3		13.21, 12.66		15.18
N–CH_3			34.9	
C_{aromat}	135.6, 130.3, 128.6, 121.2		143.7, 130.5, 127.7, 126.1	143.9, 142.0, 130.1, 128.5, 127.1

[a] $\Delta < 1.0$ are neglected.[6]

with graphite-monochromated Mo K_α radiation. The data were collected at rt using the ϖ 20 scan technique. The intensity of the control reflections varied by less than 3%, and the linear correction factor was applied to account for the effect. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs.

The structure was solved by direct methods[13] and refined using SHELXL.[14] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted *R* factors *wR* and all goodness-of-fit *S* values are based on F^2. Conventional *R* factors are based on *F* with *F* set to zero for negative F^2. The $F_o^2 > 2s(F_o^2)$ criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from International Tables for X-ray Crystallography.[15]

^{13}C NMR spectra were recorded on a Bruker MSL-300 instrument at 75.5 MHz for the $CDCl_3$ 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.

4. Supplementary material

Full crystallographic details, except the structure features, 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.csdc.cam.ac.uk). Deposition numbers CCDC 159138 (**1**), 159139 (**2**), 159140 (**3**) and 159141 (**4**).

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