

UDC 547.495:547.93

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## STRUCTURE OF *N*-ACETOXY-*N*-BENZYLOXYUREA

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The crystal structure of *N*-acetoxy-*N*-benzyloxyurea has been studied by single crystal X-ray diffraction study. It has demonstrated that this compound is a typical anomeric amide. ON(1)O nitrogen atom has a pyramidal configuration; the sum of the bond angles centered on N(1) atom is 335.2° and this atom is sp<sup>3</sup> hybridized. The N(2) nitrogen atom of the carbamoyl moiety (H<sub>2</sub>NC=O) has planar configuration. The N–OAc bond is somewhat elongated and the N–OBn bond is shortened due to the action of n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub> anomeric effect. In the molecule of *N*-acetoxy-*N*-benzyloxyurea, the N–C amide bonds are nonequivalent, and the (AcO)(BnO)N–C(O) bond is longer than the H<sub>2</sub>N–C(O) bond. Evidently, that this difference in bond lengths is caused by the stronger conjugation between lone pair (Lp) of the N(2) atom and the C=O carbonyl compared to conjugation between the lone pair of N(1) atom and the C=O carbonyl. The overall analysis of the structural parameters on all known *N*-acyloxy-*N*-alkoxyureas had been done. In addition, the structural parameters of *N*-acetoxy-*N*-benzyloxyurea have been compared with the same structural parameters of *N*-benzyloxyurea and *N*-benzyloxy-*N*-methoxyurea.

**Keywords:** *N*-acyloxy-*N*-alkoxyureas, anomeric amides, structure, single crystal X-ray diffraction study, anomeric effect.

DOI: 10.32434/0321-4095-2024-155-4-88-94

### Introduction

It is well known that the nitrogen atom in the common amides is sp<sup>2</sup> hybridized and has the planar configuration. However, the amides bearing two electronegative atoms on the nitrogen atom exhibit a special complex of the structural properties. Glover [1–9] had labeled them as «anomeric amides». In anomeric amides, the amide nitrogen responds to the collective electronegativity of the substituents by the rehybridizing from sp<sup>2</sup> to sp<sup>3</sup> [1]. Thus, the pyramidal configuration of the amide nitrogen atom in *N*-X-*N*-alkoxyamides (X=OC(O)R, OAlk, Cl) is favorable to the realization of n<sub>OAlk</sub>→σ\*<sub>N–X</sub> anomeric effect [1] and the weakening of the N–X bond [1–10]. The

pyramidal of the amide nitrogen was proved for *N,N*'-diacyl-*N,N*'-dialkoxyhydrazines [2], *N*-acyloxy-*N*-alkoxybenzamides [3], *N,N*-dialkoxybenzamides [4], *N*-alkoxy-*N*-chlorobenzamides [5], *N*-acyloxy-*N*-alkoxyureas [6–8], *N*-acyloxy-*N*-alkocarbamates [6], *N*-alkoxy-*N*-chloroureas [8], *N,N*-dialkoxyureas [7,9], *N*-alkoxy-*N*-chloro-*N*'-arylureas [9], and *N,N*-dialkoxy-*N*'-arylureas [10]. In addition, the pyramidal of amide nitrogen had been found for the salts of *N*-alkoxy-*N*-(1-pyridium)ureas and *N*-alkoxy-*N*-(1-pyridium)carbamates [7,11].

For *N*-X-*N*-alkoxybenzamides (X=OC(O)R, OAlk, Cl), the elongation of the N–X bond and the shortening of N–OAlk bond had been found [1–4].

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In addition, for *N-X-N*-alkoxyureas ( $X=OC(O)R$ , OAlk, Cl,  $N^+C_5H_4R'$ ,  $R'=H$ ,  $NMe_2$ ), these bonds deformation had been proved by XRD study [6–10].

In the *N-X-N*-alkoxybenzamides ( $X=OC(O)R$ , Cl) and *N-X-N*-alkoxyureas ( $X=OC(O)R$ , OAlk, Cl), the nucleophilic substitution at the nitrogen atom by the action of *O,N*-nucleophiles easily occurs due to the weakening of  $N-X$  bond by the  $n_{OAlk} \rightarrow \sigma^*_{N-X}$  anomeric effect action [1,5–11].

Thus, the realization of the  $n_{OAlk} \rightarrow \sigma^*_{N-X}$  anomeric effect had been demonstrated both by the structural data and by the chemical properties of *N-X-N*-alkoxyamides.

Previously, the structure of *N*-acetoxy-*N*-methoxyurea **1** [8], *N*-acetoxy-*N*-ethoxyurea **2** [6], *N-p*-chlorobenzoyloxy-*N*-ethoxyurea **3** [8] and *N-n*-butyloxy-*N-p*-chlorobenzoyloxyurea **4** [7] (Scheme 1) had been discussed.

Surprisingly, it was found that the nature of *N*-alkoxy group in *N*-alkoxy-*N-p*-chlorobenzoyloxyureas **3** and **4** affected some structural parameters of these compounds [8].

To discuss the structural features of the *N*-acetoxy-*N*-alkoxyurea series, it was necessary to expand their number. The structural data only of *N*-acetoxy-*N*-methoxyurea **1** and *N*-acetoxy-*N*-ethoxyurea **2** had been insufficient.

Thus, the objective of our current study was to explore the structure of *N*-acetoxy-*N*-benzyloxyurea **5** by single crystal X-ray diffraction study.

### Experimental

#### Materials and equipment

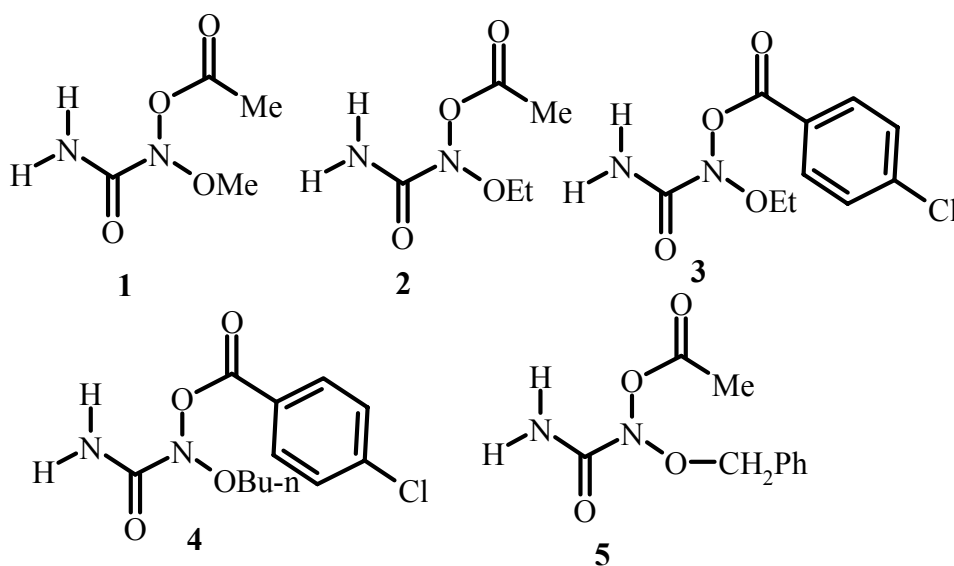
$^1H$  NMR spectra were recorded on a VARIAN VNMRS 400 spectrometer (400 MHz).  $^{13}C$  NMR

spectra were recorded on a VARIAN VNMRS 400 spectrometer (100.6117 MHz). The solvents  $CDCl_3$  and  $(CD_3)_2SO$  were used.  $^1H$  NMR chemical shifts relative to the residual solvent protons as an internal standard ( $CDCl_3$  7.260 ppm, and  $(CD_3)_2SO$  2.500 ppm) were reported. Solvent carbon atoms served as an internal standard for  $^{13}C$  NMR spectra ( $CDCl_3$  77.16 ppm). Mass spectra were recorded on a VG 70-70EQ mass spectrometer in a fast atom bombardment mode (FAB). The solvents were purified and dried according to the standard procedures.

#### Synthesis

##### *N*-Benzyloxyurea (**6**)

NaOCN (0.72 g, 10.13 mmol) was added to the mixture of  $PhCH_2ONH_2 \cdot HCl$  (0.879 g, 5.310 mmol), water (14 ml) and ether (30 ml) at stirring under  $1-2^\circ C$ ; the reaction mixture was stirred under  $4^\circ C$  for 1 h, then under  $10^\circ C$  for 1 h, then acetic acid (0.4 ml) was added and the reaction mixture was stirred at  $20^\circ C$  for 2 h. The solid was filtered off, extracted by ether ( $5 \times 40$  ml). The combined ether extracts and the filtrates were evaporated under vacuum (20 mm Hg); the residue was maintained under 2 mm Hg and  $20^\circ C$  for 1 h. The obtained residue was washed by cold ether (5 ml) and dried under vacuum (2 mm Hg), yielding *N*-benzyloxyurea **6** (0.46 g, 50%) as colorless crystals, mp.  $134-135^\circ C$ , after crystallization acetone-hexane mp.  $139-141^\circ C$  (cf. with mp.  $140-142^\circ C$  [12]).  $^1H$  NMR (400 MHz,  $(CD_3)_2SO$ , ppm):  $\delta=4.711$  (2H, s,  $NOCH_2$ ); 6.322 (2H, br. s,  $C(O)NH_2$ ); 7.286–7.439 (5H, m, Ph); 9.004 (1H, s, NHO).  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm):  $\delta=4.832$  (2H, s,  $NOCH_2$ ); 5.251 (2H, br. s,  $C(O)NH_2$ ); 7.130 (1H, s, NHO); 7.359–7.432 (5H,



Scheme 1. The discussed *N*-acyloxy-*N*-alkoxyureas

m, Ph).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta=78.97$   $\text{NOCH}_2$ ; 128.95 C(3)H, C(5)H Ph; 129.10 C(4)H Ph; 129.33 C(2)H, C(6)H Ph; 135.28 C(1) Ph; 160.88 C=O.

*N*-Benzyloxy-*N*-chlorourea (7)

The solution of *tert*-butylhypochlorite (105 mg, 0.975 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) was added to the mixture of *N*-benzyloxyurea **6** (54 mg, 0.325 mmol) and  $\text{CH}_2\text{Cl}_2$  (3 ml) at stirring at  $15^\circ\text{C}$ ; the obtained solution was stirred in the dark for 30 min. Then the solvent was evaporated under vacuum (20 mm Hg); the residue was maintained under 2 mm Hg and  $15^\circ\text{C}$  for 1 h, washed by hexane, and maintained under 2 mm Hg, yielding *N*-benzyloxy-*N*-chlorourea **7** (54 mg, 83%) as colorless solid, mp.  $70\text{--}71^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2\text{--C}_6\text{H}_{14}$ ) (with decomp.).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta=5.006$  (2H, s,  $\text{NOCH}_2$ ); 5.506 (1H, br. s, C(O)NH<sub>2</sub>); 5.896 (1H, br. s, C(O)NH<sub>2</sub>); 7.400 (5H, s, Ph).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta=77.29$   $\text{NOCH}_2$ ; 128.98 C(3)H, C(5)H Ph; 129.45 C(4)H Ph; 129.73 C(2)H, C(6)H Ph; 133.84 C(1) Ph; 160.85 C=O. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1720 (C=O). Anal. calc. for  $\text{C}_8\text{H}_9\text{ClN}_2\text{O}_2$ : Cl 17.67%. Found, Cl 17.49%.

*N*-Acetoxy-*N*-benzyloxyurea (5)

The solution of *N*-benzyloxy-*N*-chlorourea **7** (0.155 g, 0.774 mmol) in acetonitrile (9 ml) was added to the mixture of AcONa (0.159 g, 1.935 mmol) and acetonitrile (5 ml) at stirring. The reaction mixture was stirred at  $15^\circ\text{C}$  for 29 h; then  $\text{CH}_2\text{Cl}_2$  (6 ml) was added, the precipitate was filtered off and washed by  $\text{CH}_2\text{Cl}_2$  (4 ml). The combined filtrate was evaporated under vacuum (20 mm Hg), then the residue was maintained under  $20^\circ\text{C}$  and 2 mm Hg. The obtained residue was crystallized from the mixture «ether–hexane», yielding *N*-acetoxy-*N*-benzyloxyurea **5** (0.098 g, 56.5%) as colorless crystals, mp.  $68\text{--}69^\circ\text{C}$  ( $\text{Et}_2\text{O--C}_6\text{H}_{14}$ ) (with decomp.).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta=2.136$  (3H, s, NOAc); 5.083 (2H, s,  $\text{NOCH}_2$ ); 5.293 (1H, br. s, C(O)NH<sub>2</sub>); 5.771 (1H, br. s, C(O)NH<sub>2</sub>); 7.346–7.442 (5H, m, Ph).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta=18.96$  Me; 78.06  $\text{NOCH}_2$ ; 128.94 C(3)H, C(5)H Ph; 129.22 C(4)H Ph; 129.59 C(2)H, C(6)H Ph; 134.86 C(1) Ph; 159.84  $\text{H}_2\text{N(C=O)N}$ ;

168.72  $\text{NOC=O}$ . IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3486 (NH); 1800 (C=O); 1745 (C=O). MS spectrum (FAB, NaCl),  $m/z$  ( $I_{\text{rel}}$ , %): 247 [ $\text{M}+\text{Na}$ ]<sup>+</sup> (100). Anal. calc. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$ : C 53.57%; H 5.39%; N 12.49%. Found: C 53.25%; H 5.34%; N 12.29%.

*X*-ray diffraction study

The colorless crystals of compound **5** ( $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$ ), are monoclinic, from ether–hexane. At  $-100.5^\circ\text{C}$ ,  $a=10.8839(12)$  Å,  $b=7.6065(9)$  Å,  $c=14.1706(15)$  Å,  $\beta=108.527(6)^\circ$ ,  $V=1112.4(2)$  Å<sup>3</sup>,  $M_r=224.22$ ,  $Z=4$ , space group  $\text{P}2_1/c$ ,  $d_{\text{calc}}=1.339$  g/cm<sup>3</sup>,  $\mu(\text{MoK}_\alpha)=0.105$  mm<sup>-1</sup>,  $F(000)=472$ .

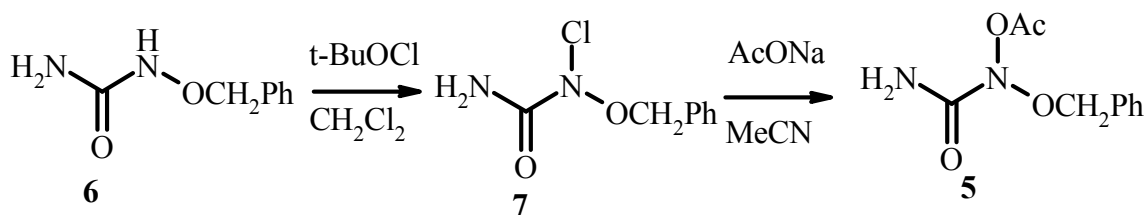
Intensities of 15044 reflections (1954 independent,  $R_{\text{int}}=0.0436$ ) were measured on the «Bruker APEX-II CCD» diffractometer (graphite monochromated  $\text{MoK}_\alpha$  radiation, CCD detector,  $\varphi$  and  $\omega$ -scanning,  $2\theta_{\text{max}}=50^\circ$ ). The structure was solved by direct method using SHELXTL package [13]. Positions of the hydrogen atoms were located from electron density difference maps and refined by «riding» model with  $U_{\text{iso}}=nU_{\text{eq}}$  ( $n=1.5$  for methyl groups and  $n=1.2$  for other hydrogen atoms) of the carrier atom. Positions of the hydrogen atoms of amino group were located in isotropic approximation. Full-matrix least-squares refinement against  $F^2$  in anisotropic approximation for non-hydrogen atoms using 1954 reflections was converged to  $wR_2=0.1252$  ( $R_1=0.0464$  for 1438 reflections with  $F>4\sigma(F)$ ,  $S=1.025$ ).

The atomic coordinates, molecular geometry parameters, and crystallographic data of compound **5** are preserved at the Cambridge Crystallographic Data Center, 12 Union Road, CB2, 1EZ UK [fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk and are available on request quoting the deposit number CCDC 2331644.

**Results and discussion**

*Synthesis and identification*

We synthesized *N*-benzyloxy-*N*-chlorourea **7** by *tert*-butylhypochlorite chlorination of *N*-benzyloxyurea **6**. The *N*-benzyloxy-*N*-chlorourea **7** interaction with anhydrous sodium acetate by known methodic [11] gives *N*-acetoxy-*N*-benzyloxyurea **5** with the moderate yield (Scheme 2).



Scheme 2. Synthesis of *N*-acetoxy-*N*-benzyloxyurea **5**

The structure of *N*-benzyloxy-*N*-chlorourea **7** and *N*-acetoxy-*N*-benzyloxyurea **5** has been proved by the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR spectra and mass spectra (Tables 1 and 2). In addition, the structure of *N*-acetoxy-*N*-benzyloxyurea **5** has been studied by the single crystal X-ray diffraction (XRD) study (Figure and Table 3).

The  $^1\text{H}$  NMR spectra of compounds **5** and **7** show such a common characteristic as the signals of the carbamoyl moiety and the singlet of  $\text{NOCH}_2$ -group (Table 1). In addition, for *N*-acetoxy-*N*-benzyloxyurea **5**, a characteristic singlet of *N*-acetoxy group has been registered [11].

Table 1

Typical  $^1\text{H}$  NMR chemical shifts of hydrogen atoms of *N*-X-*N*-benzyloxyureas **5–7** (in  $\text{CDCl}_3$ )

X, compound	Shift, ppm		
	$\text{NOCH}_2$ , s	$\text{NH}_2$ ,	$\text{NOAc}$ , s
OAc, <b>5</b>	5.083	5.293 br.s, 5.771 br.s	2.136
Cl, <b>7</b>	5.006	5.506 br.s, 5.896 br.s	–
H, <b>6</b>	4.832	5.251 br.s	–

It should be noted that the hydrogen atoms of the carbamoyl  $\text{H}_2\text{NC}(\text{O})$ -group are nonequivalent in anomeric *N*-X-*N*-benzyloxyureas **5** and **7**. Their signals are the two broadening singlets. This phenomenon has not been observed before and registered for usual *N*-benzyloxyurea **6**.

The  $^{13}\text{C}$  NMR spectra of compounds **5** and **7** show such a common characteristic as the signals of the carbon atoms of the carbamoyl and the  $\text{NOCH}_2$ -group (Table 2). In addition, the signal of carbon atom of *N*-acetoxy carbonyl has been registered for *N*-acetoxy-*N*-benzyloxyurea **5**.

Table 2

Typical  $^{13}\text{C}$  NMR chemical shifts of carbon atoms of *N*-X-*N*-benzyloxyureas **5–7** (in  $\text{CDCl}_3$ )

X, compound	Shift, ppm		
	$\text{NOCH}_2$	$\text{NH}_2\text{C}=\text{O}$	$\text{NOC}=\text{O}$
OAc, <b>5</b>	78.06	159.84	168.72
Cl, <b>7</b>	77.29	160.85	–
H, <b>6</b>	78.97	160.88	–

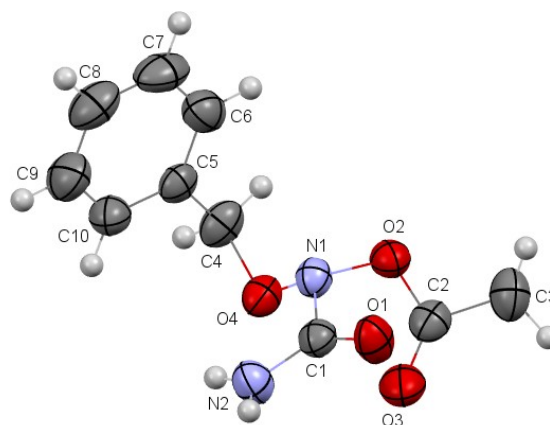
The mass spectra of compounds **5** and **7** display protonated molecular ion  $[\text{M}+\text{H}]^+$  peaks at the appropriate  $m/z$  values.

IR spectra of the compounds **5** and **7** show the bands of the carbamoyl carbonyl group  $\nu_{\text{C}=\text{O}}$  at  $1745\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$ , respectively. This is typical of the anomeric benzamides [1,5] and anomeric ureas [9].

#### Structural features

The structure of *N*-acetoxy-*N*-benzyloxyurea **5**

has many interesting peculiarities (Figure).



Molecular structure of *N*-acetoxy-*N*-benzyloxyurea **5** according to X-ray diffraction data. Thermal ellipsoids are shown at 50% probability level

In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, N(1) atom ( $\text{O}-\text{N}-\text{O}$  moiety) has pyramidal configuration. The sum of the bond angles centered on N(1) atom ( $\Sigma\beta$ ) is  $335.2^\circ$ . This phenomenon is typical of *N*-acyloxy-*N*-alkoxyureas **1–4** (Table 3) [6–8]. In the molecule of *N*-benzyloxyurea **6**, the same nitrogen atom has the planar configuration [12]. Thus, the replacement of the hydrogen atom with a acetoxy group causes the  $\text{sp}^3$  hybridization of N(1) atom, as it was predicted by Glover [1–4].

The degree of pyramidity of  $\text{O}-\text{N}-\text{O}$  nitrogen atom of *N*-acyloxy-*N*-alkoxyureas **1–5** as  $\Sigma\beta$  is presented in Table 3.

Sometimes, the influence of the nature of *N*-alkoxy moiety on the pyramidity degree of  $\text{O}-\text{N}-\text{O}$  nitrogen atom is observed [8]. The pyramidity degree of amide nitrogen atom in *N*-*n*-butyloxy-*N*-*p*-chlorobenzoyloxyurea **4** is slightly higher than the similar structural parameter of *N*-*p*-chlorobenzoyloxy-*N*-ethoxyurea **3** [8]. In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**,  $\Sigma\beta$  is slightly smaller than the  $\Sigma\beta$  value of *N*-acetoxy-*N*-methoxyurea **1** and *N*-acetoxy-*N*-ethoxyurea **2**.

In the molecule of *N*-benzyloxy-*N*-methoxyurea **8**, the configuration of the same nitrogen is pyramidal as in the compound **5**.

In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, N(2) atom (carbamoyl moiety) has planar configuration. The sum of the bond angles centered on N(2) atom ( $\Sigma\beta$ ) is  $360^\circ$ . The planar configuration of the carbamoyl nitrogen atom is caused by the conjugation between a nitrogen lone pair and  $\text{C}(1)=\text{O}(1)$  double bond. This has been observed in *N*-acyloxy-*N*-alkoxyureas **1–4** [6–8] and in *N*-benzyloxy-*N*-methoxyurea **8**.

Table 3

Typical structural parameters of *N*-acyloxy-*N*-alkoxyureas 1–5 [14], *N*-benzyloxyurea 6 and *N*-benzyloxy-*N*-methoxyurea 8

Compound	$\Sigma\beta, ^\circ$	Bond length, Å			
		N–OC(O)	N–OAlk	N <sub>sp<sup>3</sup></sub> –C(O)	H <sub>2</sub> N–C(O)
<b>1</b>	332.1	1.434(2)	1.401(2)	1.445(2)	1.317(2)
<b>2</b>	333.6	1.426(2)	1.398(2)	1.426(3)	1.330.3
<b>3</b>	329.3	1.437(1)	1.402(1)	1.459(1)	1.331(1)
<b>4</b>	323.8	1.447(2)	1.397(2)	1.441(2)	1.321(2)
<b>5</b>	335.2	1.430(2)	1.398(2)	1.432(3)	1.329(3)
<b>6</b>	360.0	–	1.406(3)	1.274(3)	1.326(3)
<b>8</b>	331.4	–	1.421(3)Bn, 1.406(3)Me	1.448(4)	1.274(3)

In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, the N–O bonds are nonequivalent. The N–OAc bond [N(1)–O(2)] is longer than the N–OBn bond [N(1)–O(4)]. These both N–O bonds are relatively shorter comparing to the average N<sub>sp<sup>3</sup></sub>–O bond length (1.463 Å) [14]. This phenomenon is typical of *N*-acyloxy-*N*-alkoxyureas **1–4** [6–8], as well as *N*-acyloxy-*N*-alkoxybenzamides [1,3]. Evidently, it is caused by the domination of n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub> anomeric effect under n<sub>O(Ac)</sub>→σ\*<sub>N–OBn</sub> anomeric effect [1].

The C(2)–O(3) bond is *sp*-oriented to the N(1)–O(2) bond (the N(1)–O(2)–C(2)–O(3) torsion angle is 3.8(3)<sup>0</sup>).

It should be noted that the length of the N(1)–O(4) bond (N–OBn bond) in the molecule of *N*-acetoxy-*N*-benzyloxyurea **5** is smaller than the length of the N–OBn bond in the molecule of *N*-benzyloxyurea **6**. However, the length of the N<sub>sp<sup>3</sup></sub>–OBn bond cannot be smaller than the length of N<sub>sp<sup>2</sup></sub>–OBn bond if the additional shortening of this N<sub>sp<sup>3</sup></sub>–OBn does not take place. In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, the observed shortening of the N–OBn bond is caused by the action of the n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub> anomeric effect.

In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, the N–C amide bonds are nonequivalent. The N(1)–C(1) bond is longer than the N(2)–C(1) one (Table 3). This phenomenon is typical of anomeric *N*-acyloxy-*N*-alkoxyureas **1–4** [6–8] and anomeric *N*-benzyloxy-*N*-methoxyurea **8** [14]. We suppose that this length difference is caused by the stronger conjugation between lone pair (Lp) of the N(2)<sub>sp<sup>2</sup></sub> atom and the C(1)=O(1) carbonyl compared to conjugation between the lone pair of N(1)<sub>sp<sup>3</sup></sub> atom and the C(1)=O(1) carbonyl bond. And vice versa, possibly, in the molecule of «nonanomeric» *N*-benzyloxyurea **6**, the conjugation between Lp of the NHO-nitrogen atom and the C=O bond is stronger than the conjugation between Lp of the NH<sub>2</sub>-nitrogen atom and the same C=O bond (Table 3).

In addition, in the molecule of *N*-acetoxy-*N*-

benzyloxyurea **5**, a significant elongation of the N(1)–C(1) bond is observed relative to this in *N*-benzyloxyurea **6** due to sp<sup>3</sup> hybridization of the N(1) nitrogen atom. The N(1)–C(1) bond is longer and the N(2)–C(1) bond is shorter as compared to the N–C bond in urea (1.350(1) Å) [15].

In *N*-acetoxy-*N*-benzyloxyurea **5**, the C(1)=O(1) bond is shortened to 1.216(2) Å (an average value is 1.23 Å [14]). This is typical of anomeric amides [1,3,9].

In the molecule of *N*-acetoxy-*N*-benzyloxyurea **5**, the carbamoyl moiety is slightly rotated with respect to the N(1)–O(2) (the O(2)–N(1)–C(1)–O(1) torsion angle is 36.0(3)<sup>0</sup>). This phenomenon is caused by the steric repulsion between C(1) and O(3) atoms. The distance between these atoms is 2.75 Å, and the appropriate sum of van der Waals radii is 3.00 Å.

The benzyl moiety is located almost orthogonally towards the N(1)–O(2) bond (the C(4)–O(4)–N(1)–O(2) torsion angle is –91.3(2)<sup>0</sup>). The phenyl group is in *–sc*-conformation relatively to the N(1)–O(4) bond and rotated to the O(4)–C(4) bond (the C(5)–C(4)–O(4)–N(1) torsion angle is –56.9(2)<sup>0</sup> and the C(10)–C(5)–C(4)–O(4) torsion angle is –70.5(3)<sup>0</sup>).

In the crystal phase, the molecules of compound **5** form the centrosymmetric dimers due to the weak intermolecular hydrogen bond N(2)–H...O1 (the symmetry operation is –x, 1–y, 1–z; the distance H...O is 2.15(3) Å, and the angle N–H...O is 165(3)<sup>0</sup>). They are connected by a weak intermolecular hydrogen bond N(2)–H...O3 (the symmetry operation is –x, 0.5+y, 0.5–z; the distance H...O is 2.50(3) Å and the angle N–H...O is 163(2)<sup>0</sup>).

### Conclusions

The structure of *N*-acetoxy-*N*-benzyloxyurea **16** has been confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, and mass spectra, as well as by the single crystal X-ray diffraction study. This study has revealed the pyramidal configuration of ONO amide nitrogen atom and its sp<sup>3</sup> hybridization. The N–OAc bond is elongated and N–OBn bond is shortened due to the n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub> anomeric effect

action. The N–C amide bonds are nonequivalent, and the (AcO)(BnO)N–C(O) bond is longer than the H<sub>2</sub>N–C(O) bond.

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Received 18.04.2024

## БУДОВА N-АЦЕТОКСИ-N-БЕНЗИЛОКСИСЕЧОВИНИ

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Кристалічна структура N-ацетокси-N-бензилоксисечовини досліджена методом рентгенівської дифракції монокристалів. Показано, що ця сполука є типовим аномерним амідом. ON(1)O атом азоту має пірамідальну конфігурацію; сума валентних кутів, центрованих на атомі N(1), становить 335.2°, і він знаходиться у стані sp<sup>3</sup> гібридизації. Атом азоту N(2) карбамільної групи (H<sub>2</sub>NC=O) має пласку конфігурацію. Зв'язок N–OAc є дещо подовженим, а зв'язок N–OBn є дещо скороченим унаслідок дії аномерного ефекту n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub>. У молекулі N-ацетокси-N-бензилоксисечовини амідні зв'язки N–C є нееквівалентні, зв'язок (AcO)(BnO)N–C(O) є довший за зв'язок H<sub>2</sub>N–C(O). Ймовірно, що ця різниця в довжині зв'язків викликана більш сильним спряженням неподіленої електронної пари атому N(2) і карбонільною групою C=O порівняно зі спряженням між неподіленою електронною парою атому N(1) і цією ж карбонільною групою C=O. Проведено загальний аналіз структурних параметрів всіх відомих N-ацетокси-N-алкоксисечовин. Структурні параметри N-ацетокси-N-бензилоксисечовини порівняні з такими самими структурними параметрами N-бензилоксисечовини та N-бензилоксисечовини-N-метоксисечовини.

**Ключові слова:** N-ацетокси-N-алкоксисечовини, аномерні амід, будова, рентгенівська дифракційне дослідження монокристалів, аномерний ефект.

STRUCTURE OF *N*-ACETOXY-*N*-BENZYLOXYUREA

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The crystal structure of *N*-acetoxy-*N*-benzyloxyurea has been studied by single crystal X-ray diffraction study. It has demonstrated that this compound is a typical anomeric amide. ON(1)O nitrogen atom has a pyramidal configuration; the sum of the bond angles centered on N(1) atom is 335.2<sup>o</sup> and this atom is sp<sup>3</sup> hybridized. The N(2) nitrogen atom of the carbamoyl moiety (H<sub>2</sub>NC=O) has planar configuration. The N–OAc bond is somewhat elongated and the N–OBn bond is shortened due to the action of n<sub>O(Bn)</sub>→σ\*<sub>N–OAc</sub> anomeric effect. In the molecule of *N*-acetoxy-*N*-benzyloxyurea, the N–C amide bonds are nonequivalent, and the (AcO)(BnO)N–C(O) bond is longer than the H<sub>2</sub>N–C(O) bond. Evidently, that this difference in bond lengths is caused by the stronger conjugation between lone pair (Lp) of the N(2) atom and the C=O carbonyl compared to conjugation between the lone pair of N(1) atom and the C=O carbonyl. The overall analysis of the structural parameters on all known *N*-acyloxy-*N*-alkoxyureas had been done. In addition, the structural parameters of *N*-acetoxy-*N*-benzyloxyurea have been compared with the same structural parameters of *N*-benzyloxyurea and *N*-benzyloxy-*N*-methoxyurea.

**Keywords:** *N*-acyloxy-*N*-alkoxyureas; anomeric amides; structure; single crystal X-ray diffraction study; anomeric effect.

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