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TWO POLYMORPHIC MODIFICATIONS OF 1-(N-MORPHOLINIOMETHYL)SPIROBI-(3-OXO-2,5-DIOXA-1-SILACYCLOPENTAN)-ATE HYDRATE

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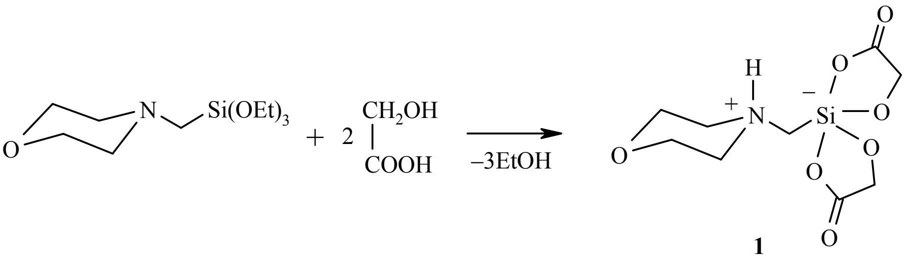
The compound 1-(N-morpholiniomethyl)spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate crystallizes from aqueous solution of γ-butyrolactone in the form of two crystal hydrate modifications: monoclinic (with D = 1.53 g/cm^3, space group $P\ 2_1/n$) and triclinic (D = 1.45 g/cm^3, space group $P\ \bar{1}$). For the monoclinic form, an X-ray structural study at -100°C has been performed. For both structures the coordination polyhedron of the silicon atom is a trigonal bipyramid. In the crystal structures there are strong intermolecular hydrogen bonds of NH···O and OH···O types.

Keywords: 1-(N-morpholiniomethyl)spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate, crystal structure, polymorphism.

1-(N-Morpholiniomethyl)spirobi(3-oxo-2,5-dioxa-1-silacyclopentan)ate (**1**) was synthesized by the action of N-morpholinomethyltriethoxysilane ether solution with glycolic acid in tetrahydrofuran. This compound is of interest as an effective and ecologically safe growth factor of plants [1].



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Usually alkoxy and acyloxy derivatives of silicon are hydrolytically unstable. However, compound **1** is stable against hydrolysis and crystallizes from aqueous solution of γ-butyrolactone (3:1) as a crystal hydrate.

At room temperature the two polymorphic modifications, namely monoclinic (**1a**) and triclinic (**1b**), crystallize simultaneously and approximately in equal quantities. The crystal structure investigation of these modifications was undertaken to study the molecular structure and to analyze the types of hydrogen bonds.

Figure 1 shows molecular diagrams of compounds **1a** and **1b** following atom numbering scheme in the text.

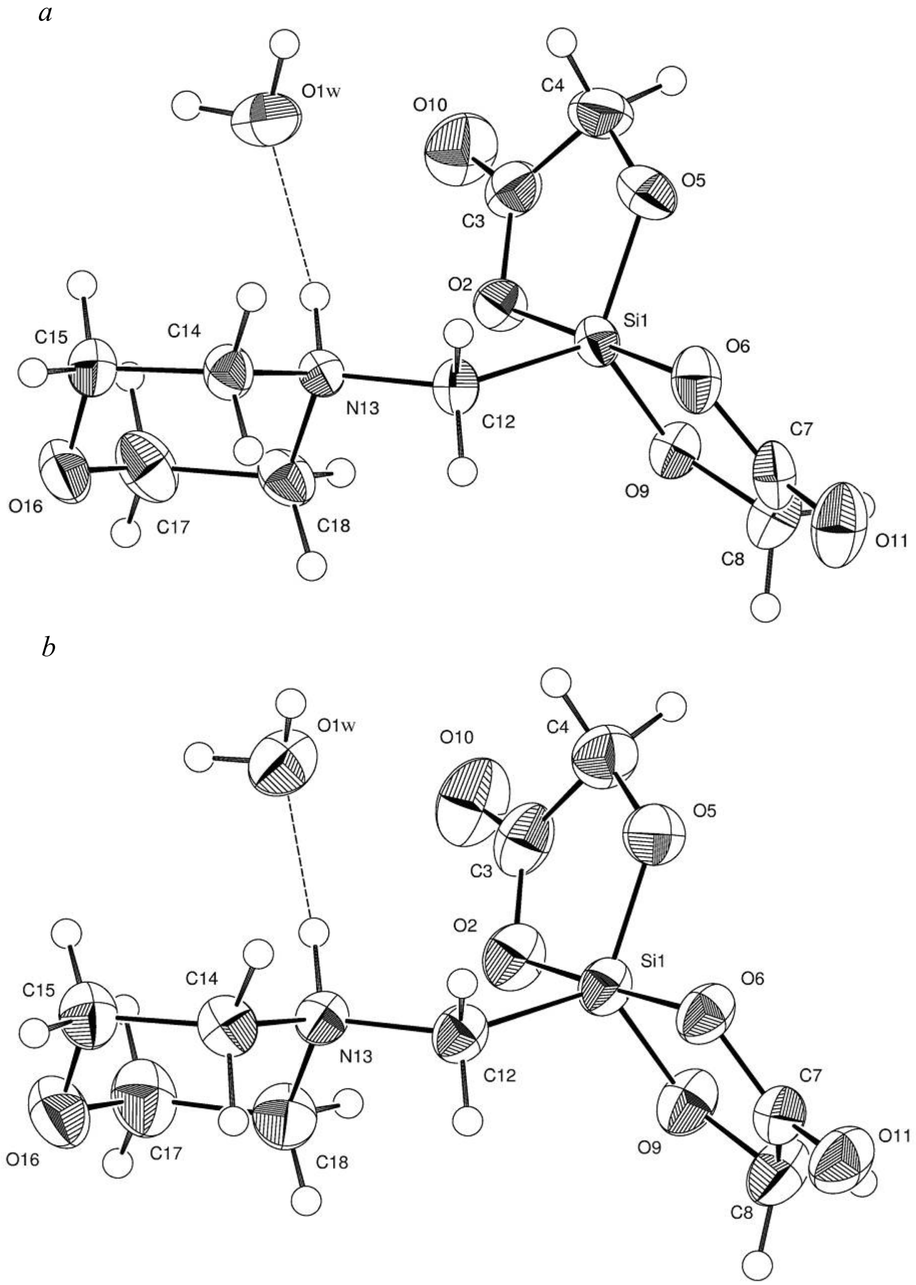

Fig. 1. The molecular structure of compounds **1a** (*a*) and **1b** (*b*) showing 50% probability displacement ellipsoids and the atom numbering scheme. H atoms are represented by spheres of arbitrary radii.

A search of the Cambridge Structural Database (CSD, Version 5.28) indicates that there are 86 entries containing spirobi(2,5-dioxa-1-silacyclopentan)ate derivatives with pentacoordinate silicon. The silicon coordination polyhedra for these compounds are trigonal bipyramids (48 entries) or square pyramids (38 entries).

The molecular structure of compound **1** in the monoclinic form is similar to that in the triclinic state. In crystals of compound **1** the silicon atom is pentacoordinate and the coordination polyhedron is a trigonal bipyramid. The silicon atom lies almost in the plane of O(5), O(9), C(12). The Si atom deviates from this plane towards atom O(2) insignificantly, -0.035(1) and 0.057(1) Å for compounds **1a** and **1b**, respectively. Tables 1 and 2 list selected bond lengths and valence angles that characterize the coordination polyhedra in compounds **1a** and **1b**. In structures of compounds **1a** and **1b** the Si−C bond is shorter than in alkylsilatranes with the C_{sp3}−Si bond [2], where the carbon atom lies in the axial position. The lengths of bonds between the silicon atom and the equatorial oxygen atoms O(5) and O(9) are significantly shorter than the axial Si−O(2) and Si−O(6) bond distances. The Si−O(2) and Si−O(6) should be described as transannular bonds in compounds **1a** and **1b**.

The estimate of the conformation of compound **1** for the isolated molecule has been undertaken by the quantum-chemical AM1 method, which is suitable for systems with hydrogen bonds [3]. Quantum-chemical calculations were performed using the MOPAC-7 program [4]. In isolated molecules of compound **1** there is an intramolecular hydrogen bond of the NH···O type between the N−H group and oxygen atom O(2). The geometrical parameters of this bond are N···O 2.844, H···O 2.089 Å, N−H···O 127.5°. The additional five-membered ring is formed in molecules of compound **1** by means of this hydrogen bond. The Si(1)−C(12)−N(13)−H(13) torsion angle is equal to -0.76° for isolated molecules.

The selected torsion angles, which characterize the molecular conformation of compounds **1a** and **1b**, are listed in Table 3. In compounds **1a** and **1b** there are strong hydrogen bonds of the NH···O type between the N−H group and oxygen of water O (1w). Therefore, the values of the Si(1)−C(12)−N(13)−H(13) torsion angle differ from the value in the isolated molecule and are equal to -45(1) and -47(1)° for compounds **1a** and **1b**, respectively. The intramolecular contacts (2.837(1) in compound **1a** and 2.936(2) Å in compound **1b**) between the N(13) and O(2) atoms should be described as a weak hydrogen bond of N(13)−H(13)···O(2),

TABLE 1. Selected Bond Lengths (*l*) for Compounds **1a** and **1b**

Bond	*l*, Å	
	1a	**1b**
Si(1)−O(2)	1.806(1)	1.796(1)
Si(1)−O(5)	1.656(1)	1.659(1)
Si(1)−O(6)	1.812(1)	1.821(1)
Si(1)−O(9)	1.663(1)	1.663(1)
Si(1)−C(12)	1.890(1)	1.893(2)

TABLE 2. Selected Valence Angles (ω) for Compounds **1a** and **1b**

Angles	ω, deg	
	1a	**1b**
O(2)−Si(1)−O(5)	89.55(5)	89.45(5)
O(2)−Si(1)−O(6)	178.71(5)	176.70(5)
O(2)−Si(1)−O(9)	89.54(5)	89.66(5)
O(2)−Si(1)−C(12)	94.42(6)	96.68(6)
O(5)−Si(1)−O(6)	90.94(6)	88.80(5)
O(5)−Si(1)−O(9)	120.79(6)	122.35(6)
O(5)−Si(1)−C(12)	118.26(6)	118.97(6)
O(6)−Si(1)−O(9)	89.18(5)	88.92(5)
O(6)−Si(1)−C(12)	86.40(6)	86.62(6)
O(9)−Si(1)−C(12)	120.82(6)	118.36(6)

TABLE 3. Selected Torsion (τ) angles for compounds **1a** and **1b**

Angles	τ, deg	
	1a	**1b**
O(2)–Si(1)–C(12)–N(13)	-3.9(1)	-8.5(1)
C(12)–Si(1)–O(2)–C(3)	121.9(1)	120.0(1)
C(14)–N(13)–C(12)–Si(1)	-160.9(1)	-163.9(1)
C(18)–N(13)–C(12)–Si(1)	76.9(2)	73.9(2)
Si(1)–C(12)–N(13)–H(13)	-44.7(10)	-46.6(11)

which occurs in isolated molecules and is stronger than in the crystal state. The H···O distances and other parameters indicate that this hydrogen bond in compound **1a** (H(13)···O(2) 2.52(1) Å, N(13)–H(13)···O(2) 102(1)°) is stronger than that in compound **1b** (H(13)···O(2) 2.69(1) Å, N(13)–H(13)···O(2) 98(1)°). Considering also the higher temperature of decomposition and denser molecular packing of compound **1a**, it can be presumed that the monoclinic modification is energetically more profitable. The packing of compound **1b** is less dense and the crystal symmetry is lower. Therefore, compound **1b** is characterized by a more profitable entropy factor. Thus, it can be concluded that the share of compound **1a** modification is increased with decreasing temperature.

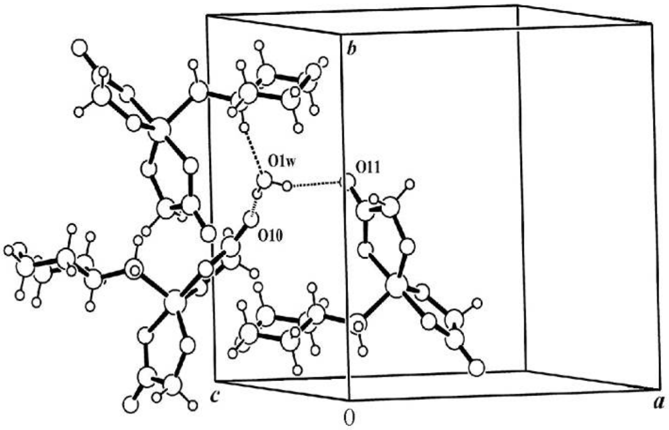

Fig. 2. Part of the crystal structure of compound **1a**, showing the formation of NH···O and OH···O hydrogen bonds.

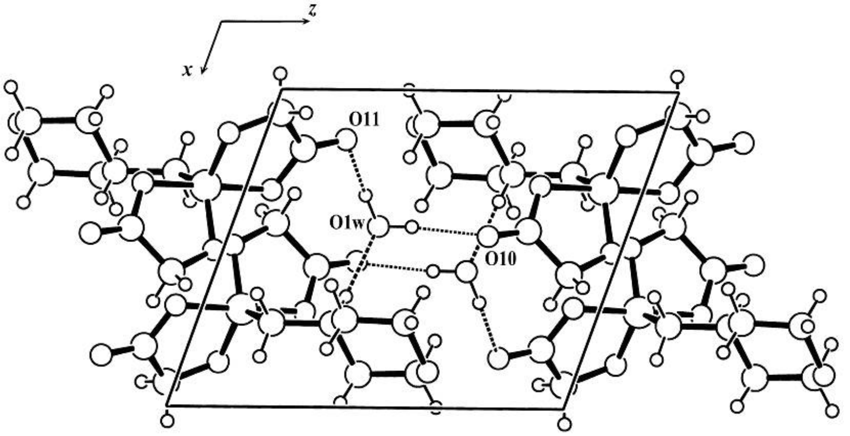

Fig. 3. Projection of the crystal structure of compound **1b** along crystallographic axis *y*, showing the formation of a hydrogen-bond net.

TABLE 4. Parameters of Intermolecular Hydrogen Bonds in Compounds **1a** and **1b**

Hydrogen bond D–H···A	D–H, Å	H···A, Å	D···A, Å	D–H···A, deg	Symmetry code for A
Compound **1a**					
N(13)–H(13)···O(1w)	0.87(2)	2.01(2)	2.849(2)	161(1)	*x*, *y*, *z*
O(1w)–H(1wA)···O(10)	0.92(3)	2.06(2)	2.953(2)	162(2)	1–*x*, –*y*, –*z*
O(1w)–H(1wB)···O(11)	0.91(3)	1.94(2)	2.838(2)	170(2)	½–*x*, *y*–½, ½–*z*
C(14)–H(14B)···O(2)	0.97(3)	2.44(2)	3.249(2)	139(2)	½+*x*, ½–*y*, ½+*z*
C(15)–H(15B)···O(11)	1.02(3)	2.45(2)	3.235(2)	133(2)	1+*x*, *y*, *z*
Compound **1b**					
N(13)–H(13)···O(1w)	0.84(2)	1.99(2)	2.824(2)	171(1)	*x*, *y*, *z*
O(1w)–H(1wA)···O(10)	0.94(3)	1.94(3)	2.868(2)	168(2)	1–*x*, 1–*y*, 1–*z*
O(1w)–H(1wB)···O(11)	0.96(3)	1.85(3)	2.800(2)	171(2)	1–*x*, 1–*y*, –*z*
C(12)–H(12B)···O(5)	1.00(3)	2.45(2)	3.411(2)	162(2)	1–*x*, 1–*y*, –*z*

Figures 2 and 3 illustrate the packing diagrams for compounds **1a** and **1b**. In the crystal structures the molecules of compound **1** with water molecules form the net of intermolecular hydrogen bonds by means of the N–H···O (N(13)–H(13)···O(1w) bond) and O–H···O (O(1w)–H(1wA)···O(10) and O(1w)–H(1wB)···O(11) bonds) type bonds. Table 4 lists the main parameters of these bonds. Except for the strong H-bonds, in the crystal structures there are shortened H···O contacts, which can be considered as weak CH···O hydrogen bonds. The parameters of these contacts are also listed in Table 4. The other intermolecular contacts correspond to the sums of van der Waals radii.

The crystal structure of the more stable monoclinic form of compound **1a** has been investigated also at low temperatures (-100ºC). The geometrical characteristics of compound **1a** at -100ºC are almost the same as at room temperature, although the unit cell parameters at lower temperatures are smaller. Accordingly, the substance density at low temperature is higher (D_{calc} = 1.560 g/ cm^3). At low temperatures lower values of the *R*-factor and standard deviations have been reached.

It was not possible to obtain diffraction data for the triclinic monocrystals of compound **1b** at low temperatures; the crystals decompose due to the phase transition. At room temperatures, both triclinic and monoclinic modifications are stable and crystallize simultaneously. In accordance with the X-ray phase analysis of the lees of compounds **1a** and **1b**, the ratio of monoclinic to triclinic phases is 55:45.

EXPERIMENTAL

For the synthesis of compound **1,** a solution of morpholinomethyltriethoxysilane (2.63 g) in diethyl ether (20 ml) was added to glycolic acid (1.52 g) in 20 ml of tetrahydrofuran. The white precipitate was filtered off and dried in air (yield 91%). Monocrystals of compounds **1a** and **1b** were obtained by slow crystallization of the substance from water–γ-butyrolactone solution (3:1) at room temperature. The separation of needle type crystals of compound **1a** and prism crystals of compound **1b** was realized manually under a microscope. The temperature of decomposition for compound **1a** is 154°C, and this value for compound **1b** is 125°C. The density of crystals of compounds **1a** and **1b** was measured by the flotation method in carbon tetrachloride–ethanol system.

Good, cut edged crystals of compounds **1a** and **1b** were used for X-ray diffraction analysis. Diffraction data were collected on a Bruker-Nonius Kappa CCD diffractometer at room temperature and also at -100°C for compound **1a**. The crystal structures were established using the SIR92 program [5]. A correction for absorption of X-rays after indexing all the facets of the crystal polyhedrons was carried out for compounds **1a** and **1b**. For

TABLE 5. Crystallographic data for compounds **1a and 1b**

	1a	**1a** (at –100°C)	**1b**
Empirical formula	$C_9H_{15}NO_7Si\cdot H_2O$	$C_9H_{15}NO_7Si\cdot H_2O$	$C_9H_{15}NO_7Si\cdot H_2O$
Formula weight	295.33	295.33	295.33
Crystal habit	Needle	Needle	Prism
Crystal size, mm	0.38×0.09×0.07	0.36 × 0.17 × 0.09	0.24 × 0.19 × 0.15
Crystal color	Colorless	Colourless	Colorless
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters			
a, Å	10.8535(3)	10.8125(3)	8.2639(3)
b, Å	11.5212(3)	11.4458(3)	8.7746(3)
c, Å	11.0284 (3)	10.9606(3)	10.6130(4)
α, deg	90.0	90.0	112.753(2)
β, deg	112.045(1)	112.033(1)	106.489(1)
γ, deg	90.0	90.0	93.554(2)
Unit cell volume, Å^3	1278.22(6)	1257.40(6)	667.54(4)
Space group	$P\,2_1/n$	$P\,2_1/n$	$P\,\bar{1}$
Z	4	4	2
F(000)	624	624	312
Density (calc.), g/cm^3	1.535	1.560	1.469
Density (meas.), g/cm^3	1.53	—	1.45
μ, mm^{-1}	0.220	0.224	0.211
$T_{\min}$	0.922	0.955	0.950
$T_{\max}$	0.985	0.980	0.969
$2\theta_{\max}$ for data, deg	55.0	55.0	55.0
Index ranges	$-14 \le h \le 14$	$-14 \le h \le 14$	$-9 \le h \le 10$
	$-13 \le k \le 14$	$-13 \le k \le 14$	$-11 \le k \le 11$
	$-14 \le l \le 14$	$-14 \le l \le 14$	$-13 \le l \le 13$
Reflection collected	4848	4977	5011
Independent reflections	2910	2974	3048
R_{int}	0.016	0.037	0.020
Reflections with $I > 2\sigma(I)$	2483	2874	2513
Final *R*-factor	0.033	0.031	0.035
R indices for all data (*R*; *wR* on F^2)	0.041; 0.095	0.041; 0.092	0.047; 0.099
Goodness of fit	1.02	1.01	1.03
Number of refined parameters	240	240	240
$(\Delta/\sigma)_{\max}$	0.001	0.001	0.001
$\Delta\rho_{\max}$	0.26	0.23	0.24
$\Delta\rho_{\text{mix}}$	-0.22	-0.22	–0.20
CCDC deposition number	CCDC 675352	CCDC 705651	CCDC 675353

calculation of transmission factors, Gaussian integration based on 8 (for compound **1a**) and 10 (for compound **1b**) indexed crystal faces was performed by the NUMABS program [6]. For refinement of the crystal structures, the SHELXL-97 program [7] was used for full-matrix least-squares calculations. For compounds **1a** and **1b** all hydrogen atoms were located by a differential Fourier map. Crystal data, conditions for data collection, and structure refinement parameters are given in Table 5.

X-ray phase analysis of powder samples was carried out on X-ray powder diffractometer Rigaku Ultima IV.

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