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CRYSTAL STRUCTURE OF 2,8,9-TRIOXA-5-AZA-1-SILABICYCLO[3.3.3]UNDEC-1-YLMETHYL-2-METHYLACRYLATE

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The XRD method is used to determine the molecular and crystal structure of 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-ylmethyl-2-methylacrylate ($H_2C{=}C(Me)C(O)OCH_2Si(OCH_2CH_2)_3N$). The crystallographic data are as follows: space group $P2_12_12_1$, $a = 9.7659(1)$ Å, $b = 10.017(1)$ Å, $c = 17.915(2)$ Å, $V = 1753.3(3)$ Å^3, $Z = 4$. The coordination polyhedron of the silicon atom is a distorted trigonal bipyramid. The length of the N→Si coordination bond is 2.099 Å.

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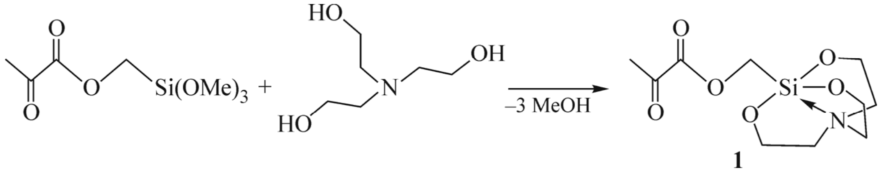
2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undec-1-ylmethyl-2-methylacrylate ((1-silatranylmethyl)methacrylate) (**1**) has long been used for manufacturing glassfibers as dipping baths, laminating agents or lubricants, increasing the adhesion of polyester and epoxy resins to glassfiber and thus increasing the elastic properties of ready fibers both while dry and wet [1]. Nevertheless, there are no data on the crystal and molecular structure of this compound in literature. We have obtained single crystals of (1-silatranylmethyl)methacrylate with a sufficient diffraction quality. The aim of this work was to determine its molecular and crystal structure.

Experimental. (1-Silatranylmethyl)methacrylate is synthesized by trans-etherification of (trimethoxysilyl)methyl-2-methylacrylate with *tris*(2-hydroxyethyl)amine.



Scheme 1.

Contrary to the previously described methods [1, 2], the reaction was carried out at room temperature and released alcohol was removed by keeping the reaction mixture under a pressure of 2 mmHg. Resulted desired product **1** is a colorless crystalline substance with T_{melt} 154-155°C (a Boëtius micro heating stage), the yield is 95%.

The elemental analysis was carried out on a FLASH 2000 CHNS analyzer, the gravimetric determination of silicon was carried out according to the procedure described in [3]. For $C_{11}H_{19}N_1O_5Si_1$ calculated (wt.%): C 48.33, H 7.01, N 5.12,

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TABLE 1. Main Interatomic Distances (*d*, Å) and Bond Angles (ω, deg) in the $H_2C{=}C(Me)C(O)OCH_2Si(OCH_2CH_2)_3N$ Molecule

Bond	*d*	Bond	*d*	Bond	*d*
Si(1)–N(1)	2.099(3)	N(1)–C(5)	1.488(6)	O(4)–C(7)	1.467(5)
Si(1)–C(7)	1.892(4)	C(1)–C(2)	1.498(7)	O(4)–C(8)	1.331(5)
Si(1)–O(1)	1.662(3)	C(3)–C(4)	1.501(7)	O(5)–C(8)	1.211(5)
Si(1)–O(2)	1.671(3)	C(5)–C(6)	1.505(7)	C(8)–C(9)	1.494(6)
Si(1)–O(3)	1.673(3)	O(1)–C(2)	1.428(6)	C(9)–C(10)	1.318(7)
N(1)–C(1)	1.480(6)	O(2)–C(4)	1.407(6)	C(9)–C(11)	1.485(7)
N(1)–C(3)	1.482(6)	O(3)–C(6)	1.426(5)		
Angle	ω	Angle	ω	Angle	ω
N(1)–Si(1)–C(7)	176.5(2)	O(1)–Si(1)–N(1)	85.1(1)	O(1)–Si(1)–O(3)	118.2(2)
O(1)–Si(1)–C(7)	96.5(2)	O(2)–Si(1)–N(1)	84.3(1)	O(2)–Si(1)–O(3)	120.0(2)
O(2)–Si(1)–C(7)	92.2(2)	O(3)–Si(1)–N(1)	85.1(1)	Si(1)–C(7)–O(4)	111.8(3)
O(3)–Si(1)–C(7)	96.8(2)	O(2)–Si(1)–O(1)	119.5(2)	O(4)–C(8)–O(5)	123.0(4)

Si 10.27; found: C 48.54, H 7.04, N 5.38, Si 10.09. The IR spectrum (cm^{-1}) (recorded on a Bruker Vertex 70 spectrometer in the spectral range 4000-500 cm^{-1}, KBr pellets): 1119, 1096, 1044, 1017, 945, 916, 785, 575 (silatrane fragment), 1699 (C=O), 1634 (C=C). The mass spectrum (GC-MS Agilent 5975C), *m/z* (%): 273 (9) [M^+], 215 (68), 188 (41), 130 (55).

A colorless crystal of the size 0.156×0.164×0.355 mm was isolated from the saturated solution of compound **1** in the chloroform:hexane (1:1) mixture. The X-ray diffraction study was carried out on a Bruker D8 Venture single crystal diffractometer equipped with a Photon 100 CMOS detector (MoK_α radiation, $\lambda = 0.71073$ Å, φ and ω scanning) at 100 K. The structure was solved by the direct method using the Bruker SAINT software package and refined by the full-matrix least squares technique in the anisotropic approximation for non-hydrogen atoms using the SHELXL-13 software package [4]. The absorption correction was applied using the SADABS program [5]. Hydrogen atoms were placed in geometrically idealized positions and refined isotropically as a rigid body. The main crystallographic data and XRD parameters of the experiment are as follows: $C_{11}H_{19}N_1O_5Si_1{\cdot}CHCl_3$, $M = 392.73$, orthorhombic crystal system, space group $P2_12_12_1$, $a = 9.769(1)$ Å, $b = 10.017(1)$ Å, $c = 17.915(2)$ Å, $V = 1753.3(3)$ $Å^3$, $Z = 4$, $d_{calc} = 1.492$ g/cm^3, $\mu = 0.611$ mm^{-1}, 44158 reflections were measured ($\theta_{max} = 26.990°$), including 3827 independent reflections, for 2995 reflections with $I > 2\sigma(I)$ $R_1 = 0.0557$, $wR_2 = 0.1557$, $S = 1.114$, $\Delta\rho$(max/min) = 0.429/–0.664 $e/Å^3$. The main geometric parameters of the molecule of **1** are listed in Table 1; the atomic numbering is given in Fig. 1. The CIF-file containing the complete information on the structure studied has been deposited with the Cambridge Crystallographic Data Centre, CCDC 1473736 (www.ccdc.cam.ac.uk/data_request/cif).

Results and discussion. The obtained single crystal is a crystalline solvate with chloroform, whose asymmetric unit contains one molecule of the desired compound and one $CHCl_3$ molecule. The coordination polyhedron of the silicon atom in the molecule of **1** is a distorted trigonal bipyramid, as in other silatrane molecules [6]. The silicon atom is out of the equatorial plane of the bipyramid formed by the O(1), O(2) and O(3) atoms by 0.15 Å toward the axially located C(7) atom. The ΔN nitrogen atom is by 0.383 Å out of plane formed by three framing C(1), C(3) and C(5) carbon atoms. The axial N(1)Si(1)C(7) bond angle is nearly linear. The length of the N→Si coordination bond in the molecule of **1** is within the range of values typical of weak electron-withdrawing substituents at the silicon atom. The same short interatomic N→Si distance is observed in 1-(N-heterylmethyl)silatranes (2.088-2.097 Å) that we have previously synthesized [7-12]. The lengths of all endocyclic bonds in the silatrane fragment of molecule **1** (Si–O, O–C, C–C and C–N) (Table 1) are typical of silatranes [13]. Five-membered cycles of the silatrane fragment adopt an *envelope* conformation. The methacrylic moiety of the molecule of **1** adopts a coplanar conformation in the O(4)O(5)C(7)C(8) plane, the C(9), C(10), C(11) atoms are out of the plane by maximum 0.022 Å, 0.038 Å, and 0.084 Å respectively. Interestingly, that the C(9)–C(10) double bond is relatively short,

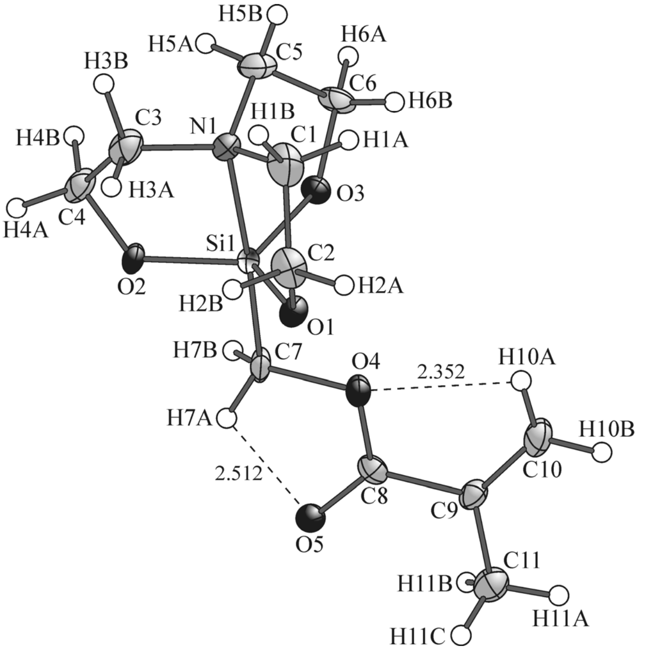

Fig. 1. Molecular structure of (1-silatranylmethyl)methacrylate **1** (atomic thermal vibration ellipsoids are drawn at the 50% probability level).

which makes it possible, according to the literature data [14], to draw the conclusion about the absence of a delocalized π system. The position of the methacrylic moiety is fixed by the intramolecular C(10)–H(10A)…O(4) (0.951 Å, 2.352 Å, 2.702(6) Å, 101.1°) and C(7)–H(7A)…O(5) (0.991 Å, 2.512 Å, 2.650(5) Å, 86.9°) hydrogen bonds.

The crystal 2D structure is formed by the intermolecular C–H…O hydrogen bonds, in which the O(5) carbonyl oxygen atom is linked with two hydrogen atoms. The C(5)–H(5B)…O(5) (0.990 Å, 2.439 Å, 3.252(6) Å, 139.0°) bond is formed *via* the methylene group proton of the silatranyl cycle of the neighboring molecule. It is this bond that is responsible for the formation of stacks parallel to the *b* axis of the unit cell, in which the neighboring molecules of silatrane **1** are oriented head-to-head. The second C(10)–H(10B)…O(5) hydrogen bond (0.950 Å, 2.360 Å, 3.274(6) Å, 161.3°), which links the molecules into a layer is formed *via* the methacrylic substituent proton of another molecule. The $CHCl_3$ molecule plays an important role in the formation of the layers. The solvate chloroform molecule in the layer is surrounded by four silatrane molecules, with one of which being linked by the intermolecular C(12)–H(12)···O(3) hydrogen bond (1.001 Å, 2.338 Å, 3.235(5) Å, 148.6°), and with another by a short C(12)–Cl(3)···O(3) contact (3.214(3) Å). Moreover, the C(2)…C(8) (3.352 Å) and C(10)…H(6A) (2.830 Å) short contacts participate in the interstack connection.

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