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Synthesis, Crystal Structure, and Spectral Characteristics of *N*-(*tert*-Butyl)aminomethanesulfonic Acid

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Abstract—A new method of the synthesis of *N*-(*tert*-butyl)aminomethanesulfonic acid in the system SO_2–$(CH_3)_3CNH_2$–CH_2O–H_2O was developed. The target compound $[(CH_3)_3C]NHCH_2SO_3H$ was characterized by means of X-ray diffraction analysis, IR spectroscopy, and mass spectrometry.

Keywords: sulfur(IV) oxide, paraformaldehyde, primary alkylamine, condensation

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Compounds of zwitterionic structure, in particular, aminoalkanesulfonic acids, their derivatives and salts [1–4] are promising components of buffer solutions [1, 2] widely used in biological research for monitoring the medium pH. Moreover, the compounds are valuable as biologically active species exhibiting various types of pharmacological activity [4, 5].

Earlier we developed an original method of synthesis of aminoalkanesulfonic acids *N*-derivatives by an example of sulfur(IV) oxide reaction with a mixture of monoethanolamine and formaldehyde in aqueous solution that led to the formation of *N*-(hydroxyethyl)-aminomethanesulfonic acid [6] (Scheme 1).

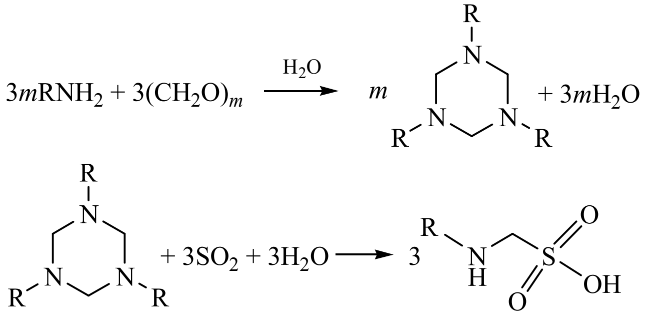
In extention of [6] we attempted the preparation of one of the *N*-derivatives of aminoalkanesulfonic acid with the use in the reaction of *tert*-butylamine. In the present report we describe the synthesis of *N*-(*tert*-butyl)aminomethanesulfonic acid and the study of its structure.

The synthesis was accomplished by the reaction of sulfur(IV) oxide with aqueous solution of a mixture of *tert*-butylamine and formaldehyde; *N*-(*tert*-butyl)aminomethanesulfonic acid was obtained in quantitative yield. The composition and structure of the target compound was confirmed by mass spectrometry, elemental analysis, IR and NMR spectroscopy, and X-ray diffraction analysis.

IR spectroscopy data of the compound indicated the zwitterionic structure similarly as for the earlier investigated analogs [6, 7].

General view of the molecule of *N*-(*tert*-butyl)aminomethanesulfonic acid is presented in Fig. 1; the values of bond lengths and bond angles are listed in Table 1.

Scheme 1.



R = CH_2CH_2OH, *t*-Bu.

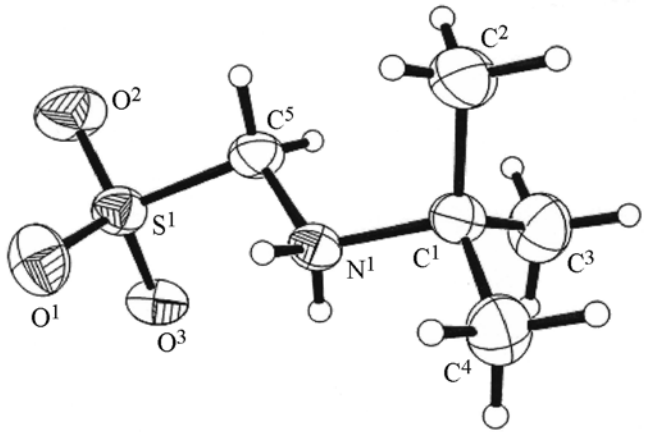


Fig. 1. General view of the molecule of *N*-(*tert*-butyl)-aminomethanesulfonic acid; thermal ellipsoids at the 50% probability level.

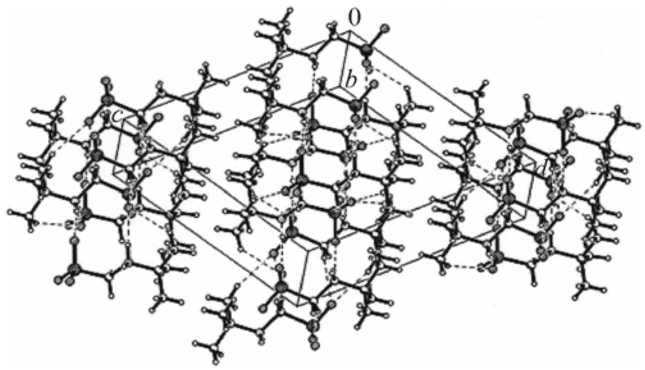


Fig. 2. Crystal packing and hydrogen bonds in the molecule of *N*-(*tert*-butyl)aminomethanesulfonic acid. Hydrogen bonds are depicted by dashed lines.

In the crystal packing of the molecules hydrogen bonds N–H···O exist between the ammonium group of one molecule and the oxygen atom of the sulfo group of the neighboring molecule that is bound with the first one through a spiral axis. Such hydrogen bonds led to the formation of infinite chains of molecules stretched along the crystallographic axis [010] (Fig. 2). There were no hydrogen bonds between the neighboring chains, only shortened interactions C–H···O were observed. Characteristics of the hydrogen bonds are given in Table 2.

Hence, a possibility of the direct synthesis of *N*-derivatives of aminomethanesulfonic acid through the condensation accompanied by oxidation S(IV)→S(VI) was confirmed by an example of the system SO_2–$(CH_3)_3CNH_2$–CH_2O–H_2O.

Table 1. Bond lengths and bond angles in the structure of *N*-(*tert*-butyl)aminomethanesulfonic acid

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
S^1–O^2	1.421(3)	$O^2S^1O^3$	113.98(18)	$N^1C^5S^1$	111.4(2)
S^1–O^3	1.453(3)	$O^2S^1O^1$	114.63(19)	$C^3C^1N^1$	109.1(3)
S^1–O^1	1.459(3)	$O^3S^1O^1$	111.14(16)	$C^3C^1C^2$	113.0(3)
S^1–C^5	1.761(4)	$O^2S^1C^5$	104.93(18)	$N^1C^1C^2$	108.0(3)
N^1–C^5	1.488(5)	$O^3S^1C^5$	106.29(18)	$C^3C^1C^4$	111.0(4)
N^1–C^1	1.521(5)	$O^1S^1C^5$	104.87(18)	$N^1C^1C^4$	105.3(3)
C^1–C^3	1.513(5)	$C^5N^1C^1$	117.3(3)	$C^2C^1C^4$	110.2(3)
C^1–C^2	1.524(5)				
C^1–C^4	1.532(5)				

EXPERIMENTAL

Commercially available sulfur(IV) oxide was used after preliminary purification and drying according to the described method [9]. *tert*-Butylamine and paraformaldehyde of “pure” grade were commercially available reagents and were used without additional purification.

IR spectra were recorded on a Spectrum BX II FT-IR System (Perkin-Elmer) spectrophotometer in the range of 4000–350 cm^{-1} from KBr pellets. Mass spectra were registered on a MX-1321 instrument (direct input of the sample into the ion source, energy of ionizing electrons 70 eV). Elemental analysis on carbon, hydrogen, and nitrogen was done on a CNH-

Table 2. Characteristics of hydrogen bonds D–H···A in the molecule of *N*-(*tert*-butyl)aminomethanesulfonic acid

D–H···A	Distance, Å			Angle DHA, deg	Coordinates of atom A
	d(D–H)	*d*(H···A)	*d*(D···A)		
$N^1H^{1A}\cdots O^1$	0.82(3)	2.03(4)	2.829(4)	166(4)	$-x + 1/2$, $y + 1/2$, $-z + 1/2$
$N^1H^{1B}\cdots O^3$	0.93(3)	1.93(3)	2.862(4)	175(3)	$-x + 1/2$, $y - 1/2$, $-z + 1/2$

analyzer; sulfur content was determined in Schoeniger flask.

X-Ray diffraction was performed on an Oxford Diffraction diffractometer (MoK_α-radiation, graphite monochromator, CCD-detector Sapphire-3). The solution and refinement of the structure were accomplished with the use of the complex of programs SHELX-97 [8]. Hydrogen atoms were found from the difference synthesis; the hydrogen atoms of methyl and methylene groups were refined according the *rider* model. The hydrogen atoms involved into hydrogen bonds were refined isotropically. The main crystallographic data and the results of the crystal refinement: $C_5H_{13}NO_3S$, monoclinic, M = 167.22, $P2_1/n$, a = 11.528(4), b = 6.4185(16), c = 12.461(5) Å; β = 116.39(5)°, V = 825.9(5) Å^3 at 293(2) K, Z = 4, d_{calc} = 1.345 g/cm, F_{000} 360, crystal 0.40 × 0.20 × 0.02 mm, μ = 0.346 mm^{-1}, λ(MoK_α) = 0.71073 Å, $T_{\min}/T_{\max}$ = 0.8740/0.9931; $-13 \le h \le 13$, $-7 \le k \le 7$, $-14 \le l \le 13$, ω-scanning at $3.66° \le \theta \le 24.98°$; 4399 measured reflections, 1331 of them were independent (R_{int} = 0.1657), and 625 were observed with $I_{hkl} > 2y(I)$, scope completeness 91.0%; full matrix refinement of 100 parameters with respect to F^2: final indicators of reliability by the observed reflections: R_F = 0.0519, wR^2 = 0.0936 (R_F = 0.1447, wR^2 = 0.1336 by all the independent reflections), S = 0.972, $\Delta\rho_{\min}/\Delta\rho_{\max}$ = –0.199/0.211 e/Å^3.

***N*-(*tert*-Butyl)aminomethanesulfonic acid.** Equimolar amount of paraformaldehyde was added to a solution of *tert*-butylamine (0.05 mol) in 20 mL of water at cooling ($t \le 10$°C); and the reaction mixture was left standing for 24 h. Then through the formed heterogenic mixture SO_2 was bubbled till pH ≤ 1.0 followed by keeping of the reaction mixture at room temperature to achieve complete evaporation of water. Yield 8.35 g (~100%), white crystals, mp 184–186°C. IR spectrum, ν, cm^{-1}: 3240 sh (NH), 3020 s, 2997 s, 2845 m, 2816 s (NH, CH); 2682 m, 2583 m, 2455 m, 2362 m (N^+H), 1624 m [$\delta(N^+H_2)$], 1487 m, 1455 m, 1435 sh, 1408 m, 1382 m, 1324 m, 1286 m, 1266 m; 1245 s, 1234 s (SO_2), 1199 sh, 1164 s; 1062 s, 1012 m (SO_2); 878 w, 852 w, 800 m, 741 m, 605 s; 549 m (S–O), 520 m, 505 sh, 472 m, 444 m, 418 w. Mass spectrum (EI), m/z (I_{rel}, %): 91 (10), 85 (13), 70 (98), 64 (87) $[SO_2]^+$, 59 (50), 57 (100) $[(CH_3)_3C]^+$, 48 (38), 41 (94), 38 (27), 30 (29). Found, %: C 35.20; H 8.31; N 8.50; S 20.05. $C_5H_{13}NO_3S$. Calculated, %: C 35.91; H 7.84; N 8.38; S 19.17. M 167.23.

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