ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 4, pp. 637–641. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © R.E. Khoma, A.A. Ennan, V.O. Gelmboldt, O.V. Shishkin, V.N. Baumer, A.V. Mazepa, Yu.E. Brusilovskii, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 4, pp. 557–561.

Preparation and Some Physicochemical Properties of Benzylammonium Sulfates

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Received June 17, 2013

Abstract—New method of preparation of multisubstituted benzylammonium cations via interaction in the SO_2–L–H_2O systems (L is benzylamine, α-phenylethylamine, *N,N*-dimethylbenzylamine, or dibenzylamine) has been developed. The products have been studied by X-ray diffraction, IR, Raman spectroscopy, and mass spectrometry.

Keywords: benzylamine, benzylammonium sulfate, X-ray diffraction, IR, Raman spectra

DOI: 10.1134/S1070363214040069

Benzylamine and its derivatives are known to form salts with inorganic [1–7] as well as organic [8–10] acids. Of these salts, nitrate [1], sulfate [2], dihydrophosphate [3], and hydroarsenate monohydrate [4] of benzylammonium; sulfate and hydrophosphate of (*S*)-α-phenylethylammonium [5]; trifluoroacetate of (*R*)-α-phenylethylammonium [8]; as well as saturated [9] and α,β-unsaturated [10] carboxylates of (±)-α-phenylethylammonium and its phenyl derivatives have been described and characterized. The interest to the abovementioned compounds is due to their possible applications. The soluble benzylammonium salts have attracted attention as drugs of enhanced bioavailability [11]; in particular, dibenzylamine forms a water-soluble antibiotic salt with penicillin [12]. Sulfate and hydrophosphate of (*S*)-1-phenylethylammonium have been studied as components of new dielectric nonlinear optical materials [5]. Salts of *N*-alkyldimethylbenzylammonium with inorganic anions have been used as antiseptics and disinfectants [13].

In this work, we describe the preparation, structure, spectral features, and thermal stability of sulfates **I**–**IV** obtained from benzylamine, α-phenylethylamine, *N,N*-dimethylbenzylamine, and dibenzylamine, respectively.

Under conditions of mass spectra detection, compounds **I**, **III**, and **IV** underwent a so-called benzyl cleavage [14]; the $[C_7H_7]^+$ peak was found in the spectra, being the most intense in the spectrum of compound **IV**.

The structure of compound **II** as determined by X-ray diffraction analysis was similar to that of benzylammonium described in [2].

The SO_4^{2-} anion is located in the particular position at the twofold axis, one $C_8H_{12}N^+$ cation and half of sulfate ion are located in the independent part of the cell (Fig. 1). The bond lengths and bond angles between the nonhydrogen atoms are collected in Tables 1 and 2. At packing in the crystal a system of hydrogen bonds is formed, their parameters are listed in Table 3. The hydrogen bonds are formed between ammonium group of the cation and oxygen atoms of sulfate ions; the bonds are located in the vicinity of the $z = 1/2$ plane, forming a layer in the $0 < z < 1$ region.

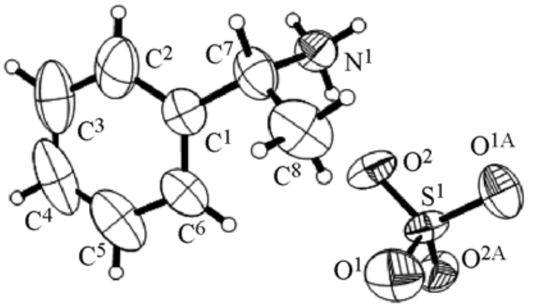

Fig. 1. General view of molecule of compounds **II** (thermal ellipsoids of probability level 50%). Symmetrically equivalent atoms are denoted as A.

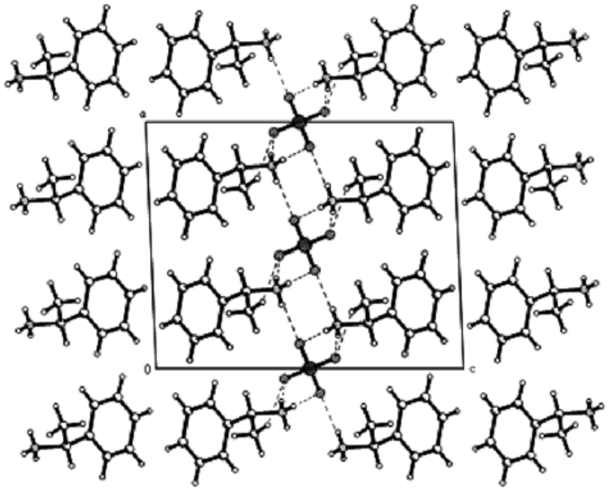

Fig. 2. Projection of molecule of compound **II** onto *x*0*z* plane. Hydrogen bonds are denoted with dashed lines.

In between these layers no hydrogen bonds are found, as shown in Fig. 2. Due to this peculiar structural feature, crystals of **II** are layered, are of poor quality and tend to twinning.

Selected parameters of IR spectra of the initial amines and compounds **I**–**IV** are shown in Table 4.

Assignment of vibration frequencies of SO_4^{2-} in IR spectrum of **I** was performed by comparison with IR spectrum of initial benzylamine and the corresponding Raman spectra taking into account the data reported in [15].

Proper assignment of the ν_{as} band of SO_4^{2-} in IR spectrum of **I** was complicated by the overlapping with vibration bands of benzylammonium cation at ~1100 cm^{-1}. However, the corresponding Raman vibrations of benzylammonium were relatively inactive, thus allowing to extract three split components of thrice degenerate asymmetric vibrations $\nu_3(F_2)$ as bands of medium (1165 cm^{-1}) and high (1093 and 1033 cm^{-1}) intensity. Hence, complication of IR spectrum of sulfate **I** as compared with that of initial amine (the appearance of a complex intense band with maximum at ~1118 cm^{-1} and a shoulder at 1160 cm^{-1} instead of a singlet band at 1145 cm^{-1} and a shoulder at 1085 cm^{-1} as well as enhancement of the band at 1030 cm^{-1}) resulted from overlap of the cation bands with $\nu_{as}(SO_4^{2-})$.

Table 1. Bond lengths in the molecule of sulfate **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S^1–O^2	1.458(5)	C^1–C^2	1.425(11)	C^4–C^5	1.366(17)
S^1–O^1	1.473(5)	C^1–C^7	1.505(10)	C^5–C^6	1.370(11)
N^1–C^7	1.525(8)	C^2–C^3	1.305(13)	C^7–C^8	1.523(12)
C^1–C^6	1.410(11)	C^3–C^4	1.429(15)		

In Raman spectrum of compound **I**, the intense band at 966 cm^{-1} was observed, absent in the spectrum of benzylamine; the band could be assigned to the full-symmetrical vibrations $\nu_s(SO_4^{2-})$. As was discussed in [15], the decrease in the symmetry of sulfate anion led to the appearance of weak full-symmetrical vibration band $\nu_1(A_1)$ in IR spectrum, its frequency being practically equal to that of the Raman band. Therefore, the newly appeared weak band at 961 cm^{-1} in IR spectrum of sulfate **I** was assigned to $\nu_s(SO_4^{2-})$ (A_1).

Table 2. Bond angles in the molecule of sulfate **II**[a]

Angle	ω, deg	Angle	ω, deg
$O^2S^1O^{2\#1}$	107.5(4)	$C^2C^3C^4$	117.4(10)
$O^2S^1O^1$	109.0(3)	$C^5C^4C^3$	118.5(10)
$O^2S^1O^{1\#1}$	110.0(3)	$C^4C^5C^6$	124.5(11)
$O^1S^1O^{1\#1}$	111.1(5)	$C^5C^6C^1$	116.7(9)
$C^6C^1C^2$	117.5(8)	$C^1C^7C^8$	114.3(7)
$C^6C^1C^7$	120.6(7)	$C^1C^7N^1$	109.8(6)
$C^2C^1C^7$	121.9(8)	$C^8C^7N^1$	108.2(6)
$C^3C^2C^1$	124.8(10)		

[a] Symmetrical transformation to get the equivalent atoms: #1 $-x + 2, y, -z + 1$.

Table 3. Parameters of hydrogen bonds D–H···A in the molecule of sulfate **II**

Bond D–H···A	Distance, Å			DHA angle, deg	Atom coordinates
	d(D–H)	*d*(H···A)	*d*(D···A)		
$N^1–H^{1A}···O^2$	0.89	1.92	2.805(8)	169.9	–*x* + 3/2, *y* + 1/2, –*z* + 1
$N^1–H^{1C}···O^2$	0.89	1.90	2.786(6)	171.6	
$N^1–H^{1B}···O^1$	0.89	1.85	2.733(8)	169.4	*x* – 1/2, *y* – 1/2, *z*

Table 4. Wavelengths (cm^{-1}) of IR absorption maxima in the spectra of starting amines and sulfates **I–IV**

Compound	ν(NH), ν(CH)	ν(N$^+$H)	δ(HN$^+$H), δ(CN$^+$H)	$\nu_{as}(SO_4^{2-})$	$\nu_s(SO_4^{2-})$	$\delta_{as}(SO_4^{2-})$	$\delta_s(SO_4^{2-})$
SO_4^{2-} free ion (T_d symmetry) [15]				1105 ν_3 (F_2, IR, Raman)	983 ν_1 (A_1, Raman)	611 ν_4 (F_2, IR, Raman)	450 ν_2 (E, Raman)
Benzylamine	3379 s, 3290 s, 3062 s, 3027 s, 2920 s, 2753 m						
I	3465 m.br, 3178 m, 2997 s, 2887 s	2676 m, 2560 m, 2341 m, 2015 m	1635 m	1160 sh, 1118 v.s, 1031 m	961 m	619 s, 573 m	471 w, 451 w
α-Phenylethylamine	3367 m, 3286 m, 3084 s, 3027 s, 2962 s, 2967 s						
II	3440 m, 3000 s.br, 2913 s.br	2752 sh, 2668 m, 2535 m, 2151 m	1635 sh, 1614 s	1134 sh, 1122 v.s, 1090 s, 1061 s	971 m	635 sh, 620 m, 588 m	465 w, 430 w
N,N-Dimethylbenzylamine	3027 s, 2893 s, 2846 s, 2804 s						
III	3406 s.br, 3038 m.br	2704m. br, 2405 m. br, 2265 m	1649 m	1140 sh, 1090 v.s, 1058 v.s, 1047 v.s	961 m	709 m, 605 w	494 w, 415 m
Dibenzylamine	3313 m, 3105 m, 3027 s, 2918 s, 2816 s						
IV	3460 m, 3061 sh, 3290 sh, 3000 v.s, 2833 m	2641 m, 2474 m, 2364 m, 2341 m	1623 m, 1615 m	1134 s.br	920 m	668 m, 658 sh, 645 m	513 sh, 415 w

Two components of thrice degenerate bending bands $\delta_{as}(SO_4^{2-})(\nu_4)$ in IR spectrum of compound **I** were observed as strong (619 cm^{-1}) and moderate intensity (573 cm^{-1}) bands. In the Raman spectra, two moderate intensity bands at 623 and 590 cm^{-1} corresponded to those IR bands, thus pointing at the $\nu_4(F_1 > A_2 + E_U)$ splitting.

In the range of twice degenerate deformation vibration ν_2 (450 cm^{-1}) of free SO_4^{2-} ion, in IR spectrum of sulfate **I** the appearance of two well defined shoulders (471 and 451 cm^{-1}) of the out-of-plane δ(CCH) bending at 485 cm^{-1} is notable. In the Raman spectrum, $\delta_s(SO_4^{2-})$ vibrations were assigned to the weak band at 446 cm^{-1}.

Bands of stretching and bending vibrations of SO_4^{2-} anion in IR spectra of sulfates **II**–**IV** were assigned by comparative analysis of spectra of the salts, of the initial benzylamines, and of compound **I**. It follows from Table 3 that the intrinsic vibrations of SO_4^{2-} ion appeared in IR spectra as the full set of possible frequencies due to splitting of the F_2 and E vibrations and activity of the A_1 vibrations; that could point at a low symmetry of the anion in the crystalline salts as compared with T_d symmetry of the free anion.

In IR spectra of the salts the range of 3500–2000 cm^{-1} contained complex bands of N–H stretching vibrations of the NH_3^+, NH_2^+, and NH^+ groups [15, 16]. Noteworthily, the bands at 2015 cm^{-1} (**I**), 2151 cm^{-1} (**II**), 2265 cm^{-1} (**III**), and 2341 cm^{-1} (**IV**) were due to strong hydrogen bonds NH···O in the crystalline salts; the presence and position of those bands in the IR spectra could characterize the participation of benzylammonium cations in the hydrogen bonding [17].

The characteristic scissor vibration bands of ammonium groups, $\delta(HN^+H)$ and $\delta(NN^+H)$, were detected in the relatively narrow region of 1650–1610 cm^{-1}.

In the thermogram of sulfate **I**, two endothermic effects were detected at 210–320°C (T_{max} 280°C, Δm 69.86%) and 390–550°C (T_{max} 460°C, Δm 7.94%) as well as an exothermic effect at 550–660°C (T_{max} 600°C, Δm 7.94%). In the thermogram of compound **II** the endothermic effect at 240–370°C (T_{max} 300°C, Δm 64.29%) was detected along with the exothermic effect at 390–660°C (T_{max} 600°C, Δm 17.03%). When in air, compounds **I** and **II** were stable, the decomposition onset being detected at 210 and 240°C, respectively; the (*S*) enantiomer **II** started decomposing at 230°C [3]. Noteworthily, the low-temperature effects in thermograms of compounds **I** and **II** corresponded to elimination of the same fragments ($M \approx 218$ g/mol), evidently showing the special feature of thermolysis of benzylammonium sulfates.

The thermogram of compound **III** contained three endothermic effects at 90–140°C (T_{max} 100°C, Δm 16.22%), 140–250°C (T_{max} 170°C, Δm 18.24%), and 300–385°C (T_{max} 350°C, Δm 46.62%) as well as an exothermic effect at 400–590°C ($T_{max} = 550$°C, $\Delta m =$ 4.05%). The thermogram of compound **IV** contained an endothermic effect at 90–150°C (T_{max} 130°C, Δm 11.92%) along with two exothermic effects at 230–360°C (T_{max} 290°C, Δm 70.86%) and 530–610°C (T_{max} 580°C, Δm 2.65%).

To conclude, this work demonstrated new examples of stabilization of sulfate anion in the form of alkylammonium salts prepared in the SO_2–L–H_2O systems (L were mixed amines) in the presence of air according to the formal scheme.

$$2SO_2 + 4R_nNH_{3-n} + 2H_2O + O_2 \rightarrow 2(R_nNH_{4-n})_2SO_4.$$

The effect was reported for the first time in [18].

The possibility of mild oxidation of SO_2 under the specified conditions will be further studied in detail involving other amine ligands.

EXPERIMENTAL

Technical grade sulfur(IV) oxide was used after purification and drying [21]. All amines were of pure grade and were used as received.

Analysis for carbon, hydrogen, and nitrogen content was performed using a CHN elemental analyzer; content of sulfur was determined using the Scheniger method [19].

Raman spectra were obtained using a DFS-24 spectrometer with excitation at 532 and 632.8 nm (neodymium and helium-neon lasers, respectively).

IR spectra were recorded using a spectrophotometer Spectrum BX II FT-IR System (Perkin-Elmer) (KBr); mass spectra were registered on a MKh-1321 instrument (direct amission of the sample into the ion source, ionizing electrons energy 70 eV).

Thermal stability of the compounds was determined by the differential thermal analysis (the Q-1500 D Paulik–Paulik–Erdey derivatograph, platinum crucible, in air, 20–1000°C at a rate 10 deg/min, sensitivity 1/5 of the maximum one, Al_2O_3 reference).

X-ray diffraction studies were performed using the Oxford Diffraction diffractometer (MoK_α radiation, graphite monochromator, CCD detector Sapphire-3). The structures were solved and refined using SHELX-97 software package [20]. Hydrogen atoms positions were found via differential analysis of electron density and refined in the *rider* model. The basic crystallographic parameters of compound **II** were as follows: $C_{16}H_{24}N_2O_4S$, monoclinic, *M* 340.43, space group *C*2, *a* 10.876(2), *b* 6.0814(10), *c* 13.609(4) Å; β 92.47(3)°, *V* 899.3(4) Å^3 at *T* 293(2) K, *Z* 2, d_{calc}

1.257 g/cm^3, F_{000} 364, crystal 0.30×0.20×0.02 mm, μ 0.200 mm^{-1} [λ(MoK_α) 0.71073 Å], transmission coefficients $T_{\min}/T_{\max}$ 0.9424/0.9960; $-6 \le h \le 13$, $-7 \le k \le 7$, $-15 \le l \le 16$, ω-scan at $3.00 \le \theta \le 25.48°$, 2410 measured reflections, 1479 independent reflections (R_{int} 0.0969), 986 reflections with $I_{hkl} > 2\sigma(I)$, coverage completeness 94.0%; final parameters of full-matrix refinement of 108 parameters according to F^2 using the 986 reflections: R_F 0.0923, wR^2 0.2041 (R_F 0.1269, wR^2 0.2286 for all independent reflections), S 1.003, $\Delta\rho_{\min}/\Delta\rho_{\max}$ –0.253/0.387 e/Å^3.

Benzylammonium sulfate (I). Gaseous SO_2 was passed through a mixture of 10 mL of benzylamine and 20 mL of water (0°C) at 50 mL/min till pH dropped below 1.0. Then the reaction mixture was isothermally evaporated at room temperature to full dehydration. The so formed solid product was washed with benzene and recrystallized from water. Yield 14.30 g (82.3%), white crystals with specific smell, mp 105–107°C. Mass spectrum, m/z (I_{rel}, %): 107 (69) $[M_L]^+$; 106 (100) $[M_L - H]^+$; 91 (13) $[C_7H_7]^+$; 78 (15); 77 (22) $[C_6H_5]^+$; 52 (8); 51 (15); 39 (7). Found, %: C 53.49; H 6.24; N 8.64; S 9.84. $C_{14}H_{20}N_2O_4S$. Calculated, %: C 53.83; H 6.45; N 8.97; S 10.26. M 312.38.

α-Phenylethylammonium sulfate (II) was prepared similarly from 10 mL of phenylethylamine and 50 mL of water. Yield 13.37 g (89.1%), white crystals (without further purification), mp 195–200°C. Mass spectrum, m/z (I_{rel}, %): 120 (8) $[M_L - H]^+$; 107 (8); 106 (100) $[M_L - CH_3]^+$; 79 (24); 77 (13) $[C_6H_5]^+$; 53 (9), 51 (10); 44 (18); 43 (7); 42 (13). Found, %: C 56.89; H 7.39; N 8.51; S 9.77. $C_{16}H_{24}N_2O_4S$. Calculated, %: C 56.45; H 7.11; N 8.23; S 9.42. M 340.44.

***N,N*-Dimethylbenzylammonium sulfate (III)** was prepared similarly from 10 mL of *N,N*-dimethylbenzylamine and 50 mL of water. Yield 10.51 g (92.8%), yellow oily liquid. Mass spectrum, m/z (I_{rel}, %): 135 (40) $[M_L]^+$; 134 (30) $[M_L - H]^+$; 92 (5); 91 (40) $[C_7H_7]^+$; 65 (13%); 58 (100); 44 (10); 42 (17). Found, %: C 59.13; H 7.41; N 7.39; S 9.05. $C_{18}H_{28}N_2O_4S$. Calculated, %: C 58.67; H 7.66; N 7.60; S 8.70. M 368.49.

Dibenzylammonium sulfate (IV) was prepared similarly from 10 mL of dibenzylamine and 50 mL of water. Yield 8.07 g (91.4%), white crystals, mp 93°C. Mass spectrum, m/z (I_{rel}, %): 198 (14) $[M_L+H]^+$; 196 (14) $[M_L - H]^+$; 120 (10); 106 (85); 105 (26); 92 (26); 91 (100) $[C_7H_7]^+$; 77 (31%) $[C_6H_5]^+$; 65 (14); 64 (17) $[SO_2]^+$; 51 (14). Found, %: C 67.73; H 6.81; N 8.61; S 6.35. $C_{28}H_{32}N_2O_4S$. Calculated, %: C 68.27; H 6.55; N 5.69; S 6.51. M 492.63.

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