



Synthesis and Characterization of 3-[N-(2-Methacroyloylethyl)-N,N-dimethylamino]propane Sulfonate and its Crystal Structure

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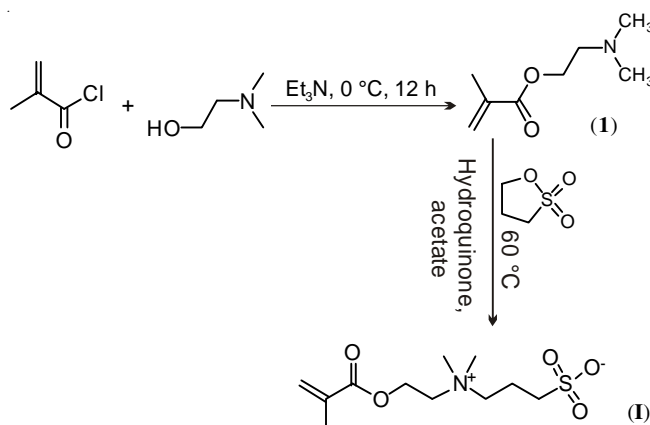
3-[N-(2-Methacroyloylethyl)-N,N-dimethylamino]propane sulfonate (DMAPS) was synthesized by the ring-opening reaction of 1,3-propanesultone, then electrophilic substitution with 2-(dimethylamino)ethyl methacrylate in the presence of acetone at 60 °C. 2-(Dimethylamino)ethyl methacrylate and a little polymerization inhibitor dissolved in acetone was added in three-necked flask, the mixture was heated to 60 °C. 1,3-Propanesultone was dissolved in acetone and then be added drop-wise into the flask over 8 h. The product was characterized by NMR and Mass spectrum. The crystal structure of 3-[N-(2-Methacroyloylethyl)-N,N-dimethylamino]propane sulfonate was investigated using X-ray diffraction and SHELXTL97 software and the result indicated that DMAPS crystallized in the orthorhombic system, space group P2₁/c with a = 14.6818(18), b = 7.1104(9), c = 14.9180(18) Å, V = 1548.5(3) Å³; Z = 4.

Keywords: 3-[N-(2-Methacroyloylethyl)-N,N-dimethylammonio]-propane sulfonate, Synthesis, Characterization, Crystal structure.

INTRODUCTION

The importance of zwitterionic compounds as biological and ships aspects has been well established¹. Some zwitterionic compounds had been reported for the surfactant, medicines and anticoagulant material, *etc.*^{2,3}. For example, 2-methacroyloxyethyl phosphorylcholine could be used for biomedical materials^{4,5}, 3-[(2-acrylamido)dimethylamino]propane sulfonate is a useful monomer in the preparation of anticoagulant material⁶.

3-[N-(2-methacroyloylethyl)-N,N-dimethylamino]-propane sulfonate (DMAPS, **I**), as one of zwitterionic compounds, could be utilized for the synthesis of different chemicals that have important application in the preparation of anticoagulant polymeric films, such as P-AM-DMAPS⁷, *etc.* 2-(dimethylamino)ethyl methacrylate (**1**) was synthesized by the method of ester exchange with tetraphenyl titanate as a catalyst⁸, (**I**) could be prepared from (**1**) with 1,3-propanesultone in the presence of acetone at 50 °C for 20 h⁹. Herein, we report DMAPS (**I**) was synthesized by methacryloyl chloride with N,N-dimethyl ethanolamine in the presence of dichloromethane at 0 °C for 12 h. (**I**) was prepared from the ring-opening reaction of 1,3-propanesultone, then electrophilic substitution with 2-(dimethyl-amino)ethyl methacrylate (**1**) in the presence of acetone at 60 °C for 8 h. Meanwhile, the crystal structure of (**I**) also was investigated. The synthesis of DMAPS presented as **Scheme-I**.



Scheme-I: Route for the synthesis of DMAPS

EXPERIMENTAL

N,N-Dimethyl ethanolamine and methacryloyl chloride were supplied by Forever Reagent Co. Ltd. of Shanghai (Shanghai, People's Republic of China), their mass content are 99 % determined by GC. 1,3-Propanesultone was supplied by Aladdin Industrial Corporation (Shanghai, People's Republic of China), its mass content is 99.0 %. All other chemicals were of reagent grade and used without purification as received.

^1H NMR spectrum was obtained with Bruker AV-300 spectrometer at 300.13 MHz and measured in D_2O solution at 20 ± 0.5 °C. The sample was dissolved in a 5 mm diameter tube at a concentration of about 20 mg/mL. X-ray diffraction was performed on a Bruker APEXII CCD diffractometer. Mass spectrum of (**I**) was analyzed using Trace DSQ GC/MS (Thermo Electron Co., USA).

Synthesis of 3-[N-(2-methacroyloylethyl)-N,N-dimethyl-amino]propane sulfonate: In a 100 mL three-necked flask, N,N-dimethyl ethanolamine (20 mmol) and triethylamine (40 mmol) were dissolved by dichloromethane in an ice-water bath. Methacryloyl chloride was dissolved in dichloromethane, then it was added into the reaction vessel slowly. After 12 h, the system was filtered. The organic layer was washed with water, saturated sodium bicarbonate solution and saturated sodium chloride solution successively. The organic layer was dried over anhydrous sodium sulfate. The product purified by column chromatography (petroleum ether:ethyl = 3:1). Compound (**I**) was obtained in the form of a colourless liquid (Yield: 75 %).

To a 250 mL three-necked flask equipped with a magnetic stirrer, condenser and dropping funnel, 0.11 mol of 2-(dimethyl-amino)ethyl methacrylate (**1**) and a little hydroquinone dissolved in 30 mL acetone was added and the mixture was heated to 60 °C in a thermostated water bath. 0.1 mol of 1,3-propanesultone was dissolved in 30 mL acetone was added and then added drop-wise in to the flask over 8 h under magnetic stirring, subsequently react at 60 °C for 2 h. The DMAPS was precipitated from the reaction medium in the form of white crystal, separated by filtration, vigorously washed with acetone. After filtration, the fine compound (**I**) was obtained by recrystallization of the filter residue using absolute ethanol as solvent. Crystals of (**I**) that suitable for X-ray diffraction were obtained by slow evaporation of 95 % ethanol solution of (**I**).

X-ray crystallography: A colourless block-like crystal of compound (**I**) grown in 95 % ethanol with dimensions of 0.27 mm \times 0.20 mm \times 0.16 mm was used for structural determination. Diffraction data were collected on a Bruker APEXII CCD diffractometer by using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SHELXS-97 and refined on the F^2 by full-matrix least-squares method with SHELXL-97. All non-hydrogen atoms were refined anisotropically.

RESULTS AND DISCUSSION

Identification of resonance in the spectra: In the ^1H NMR spectrum of DMAPS, the peaks at 6.03 ppm and 5.65 ppm were due to the proton of olefin double bond, 4.70 ppm was assigned to the proton of D_2O . The peaks at 4.51, 3.70, 3.50, 2.84 and 2.04 ppm were assigned to the H of CH_2 group, the peak at 3.09 and 1.80 ppm were assigned to the H of CH_3 group. In the MS spectrum, the m/z 280 was assigned to molecular ion peak ($M+1$).

The crystal configuration of DMAPS was confirmed by X-ray structural analysis. Experimental details for X-ray data collection were presented in Table-1 and the geometric parameters for compound (**I**) were listed in Table-2. Molecular structure and packing plot of DMAPS were showed in Figs. 1 and 2, respectively.

TABLE-1 CRYSTALLOGRAPHIC DATA FOR COMPOUND (I)	
Item	Data or description
Formula	$\text{C}_{11}\text{H}_{23}\text{NO}_6\text{S}$
Formula weight	297.36
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.6818(18)
b (Å)	b = 7.1104(9)
c (Å)	c = 14.9180(18)
Volume (Å ³)	1548.5(3)
Z	4
Calculated density (g/cm ³)	1.276
Absorption coefficient (mm ⁻¹)	0.23
F(000)	640
Crystal size (mm)	0.27 \times 0.20 \times 0.16
Theta range for data collection (°)	1.4 to 27.5
Reflections collected/unique	3495/2944 [R(int) = 0.108]
Completeness to $\theta = 25.39$ (%)	99.9
Max. and min. transmission	0.9407 and 0.9642
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3495/15/175
Goodness-of-fit on F^2	1.05
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0548, wR2 = 0.1546
R indices (all data)	R1 = 0.0625, wR2 = 0.1639
Largest diff. peak and hole (e. Å ⁻³)	0.63 and -0.48

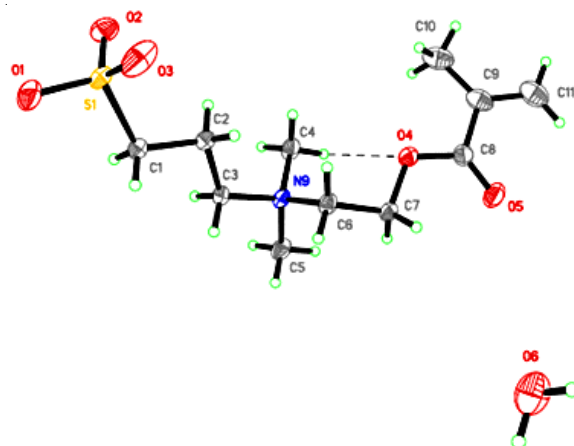


Fig. 1. General appearance of compound **I** with the atoms represented by thermal vibration ellipsoids of 50 % probability

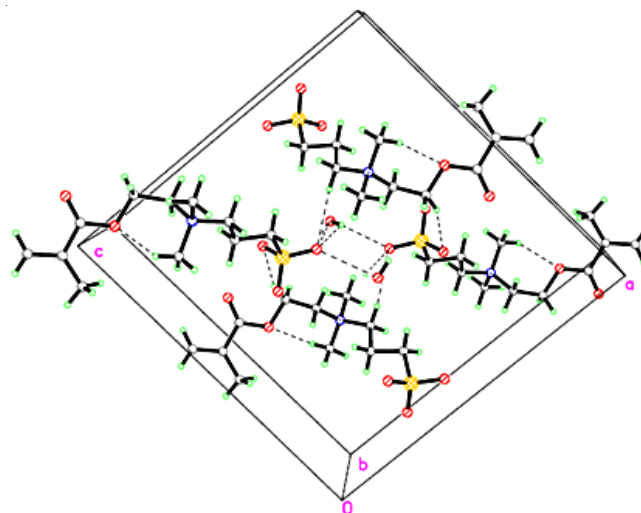


Fig. 2. Packing diagram for compound **I**

TABLE-2
GEOMETRIC PARAMETERS FOR COMPOUND (I)

Bond	Dist. (Å)	Bond	Dist. (Å)
C1–C2	1.523 (2)	C6–H6A	0.9700
C1–S1	1.7690(18)	C6–H6B	0.9700
C1–H1A	0.9700	C7–O4	1.447(2)
C1–H1B	0.9700	C7–H7A	0.9700
C2–C3	1.525 (2)	C7–H7B	0.9700
C2–H2A	0.9700	C8–O5	1.198 (3)
C2–H2B	0.9700	C8–O4	1.345 (3)
C3–N9	1.521(2)	C8–C9	1.491 (3)
C3–H3A	0.9700	C9–C11	1.368 (5)
C3–H3B	0.9700	C9–C10	1.446 (5)
C4–N9	1.497(2)	C10–H10A	0.9600
C4–H4A	0.9600	C10–H10B	0.9600
C4–H4B	0.9600	C10–H10C	0.9600
C4–H4C	0.9600	C11–H11A	0.9300
C5–N9	1.507(2)	C11–H11B	0.9300
C5–H5A	0.9600	O1–S1	1.4589 (17)
C5–H5B	0.9600	O2–S1	1.4406 (16)
C5–H5C	0.9600	O3–S1	1.4380 (17)
C6–N9	1.509 (2)	O6–H6D	0.8500
C6–C7	1.510 (3)	O6–H6C	0.8499
Angle	Data (°)	Angle	Data (°)
C2–C1–S2	113.56 (13)	O4–C7–C6	108.62 (16)
C2–C1–H1A	108.9	O4–C7–H7A	110.0
S1–C1–H1A	108.9	C6–C7–H7A	110.0
C2–C1–H1B	108.9	O4–C7–H7B	110.0
S1–C1–H1B	108.9	C6–C7–H7B	110.0
H1A–C1–H1B	107.7	H7A–C7–H7B	108.3
C1–C2–C3	106.61 (14)	O5–C8–O4	122.3 (2)
C1–C2–H2A	110.4	O5–C8–C9	124.5(2)
C3–C2–H2A	110.4	O4–C8–C9	113.1 (3)
C1–C2–H2B	110.4	C11–C9–C10	124.2 (3)
C3–C2–H2B	110.4	C11–C9–C8	116.3 (3)
H2A–C2–H2B	108.6	C10–C9–C8	119.5 (3)
N9–C3–C2	116.53 (14)	C9–C10–H10A	109.5
N9–C3–H3A	108.2	C9–C10–H10B	109.5
C2–C3–H3A	108.2	H10A–C10–H10B	109.5
N9–C3–H3B	108.2	C9–C10–H10C	109.5
C2–C3–H3B	108.2	H10A–C10–H10C	109.5
H3A–C3–H3B	107.3	H10B–C10–H10C	109.5
N9–C4–H4A	109.5	C9–C11–H11A	120.0
N9–C4–H4B	109.5	C9–C11–H11B	120.0
H4A–C4–H4B	109.5	H11A–C11–H11B	120.0
N9–C4–H4C	109.5	C4–N9–C5	109.26 (16)
H4A–C4–H4C	109.5	C4–N9–C6	111.73 (15)
H4B–C4–H4C	109.5	C5–N9–C6	110.40 (14)
N9–C5–H5A	109.5	C4–N9–C3	110.04 (14)
N9–C5–H5B	109.5	C5–N9–C3	105.70 (15)
H5A–C5–H5B	109.5	C6–N9–C3	109.54 (13)
N9–C5–H5C	109.5	C8–O4–C7	115.31 (16)
H5A–C5–H5C	109.5	H6D–O6–H6C	108.1
H5B–C5–H5C	109.5	O3–S1–O2	113.00 (13)
N9–C6–C7	116.84 (15)	O3–S1–O1	111.94 (13)
N9–C6–H6A	108.1	O2–S1–O1	112.11 (11)
C7–C6–H6A	108.1	O3–S1–C1	107.28 (10)
N9–C6–H6B	108.1	O2–S1–C1	107.06 (10)
C7–C6–H6B	108.1	O1–S1–C1	104.86 (10)
H6A–C6–H6B	107.3		
S1–C1–C2–C3	-173.05 (13)	C2–C3–N9–C4	-59.8 (2)
C1–C2–C3–N9	-175.76 (15)	C2–C3–N9–C5	-177.62 (16)
N9–C6–C7–O4	76.9 (2)	C2–C3–N9–C6	63.44 (19)
O5–C8–C9–C11	-5.5 (4)	O5–C8–O4–C7	0.5 (3)
O4–C8–C9–C11	174.2 (2)	C9–C8–O4–C7	-179.25 (17)
O5–C8–C9–C10	174.2 (2)	C6–C7–O4–C8	167.92 (17)
O4–C8–C9–C10	-6.0 (3)	C2–C1–S1–O3	-60.14 (18)
C7–C6–N9–C4	-62.3 (2)	C2–C1–S1–O2	61.43 (17)
C7–C6–N9–C5	59.5 (2)	C2–C1–S1–O1	-179.31 (15)
C7–C6–N9–C3	175.54 (15)		

According to the data from X-ray crystallographic analysis, compound (I) crystallized in a $P2_1/c$ space group of the monoclinic system. The only H atom was positioned geometrically and constrained to ride on C1 with $C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. Hydrogen-bond geometry for compound (I) was listed in Table-3. Unit cell parameters: $a = 14.6818(18)$, $b = 7.1104(9)$, $c = 14.9180(18) \text{ \AA}$, $V = 1548.5(3) \text{ \AA}^3$; $Z = 4$.

TABLE-3
HYDROGEN-BOND GEOMETRY FOR COMPOUND (I)

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O6–H6C...O1i	0.85	2.36	2.816 (3)	114
O6–H6C...O1ii	0.85	2.39	2.902 (3)	119
C1–H1B...O6iii	0.97	2.44	3.383 (3)	163
C3–H3A...O1iv	0.97	2.55	3.476 (3)	159
C3–H3B...O3v	0.97	2.55	3.392 (3)	145
C4–H4A...O4	0.96	2.46	2.958 (2)	112
C4–H4C...O3v	0.96	2.41	3.272 (3)	149
C5–H5A...O3v	0.96	2.50	3.342 (3)	146
C5–H5C...O2vi	0.96	2.39	3.308 (3)	160
C7–H7A...O3vii	0.97	2.55	3.472 (3)	159
C7–H7B...O2vi	0.97	2.59	3.546 (3)	170
C11–H11A...O2viii	0.93	2.42	3.309 (4)	159

Symmetry code: (i) $x, y, z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, y+1/2, -z+1$; (v) $x, y+1, z$; (vi) $x, -y+1/2, z-1/2$; (vii) $x, -y-1/2, z-1/2$; (viii) $-x, y+1/2, -z+1/2$

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