DAEHAN HWAHAK HWOEJEE
(*Journal of the Korean Chemical Society*)
Vol. 32, No. 4, 1988
Printed in the Republic of Korea

암모늄 파라-메칠벤젠슬폰네이트의 결정 및 분자구조

安重泰†, **Gene B. Carpenter***
한국외국어대학교 문리과대학 화학과
서울 동대문구 이문동 271-1
(1987. 11. 18 접수)

The Crystal and Molecular Structure of Ammonium *p*-Methylbenzenesulfonate

Choong Tai Ahn† and Gene B. Carpenter*
Department of Chemistry, College of Liberal Arts & Sciences,
Hankuk University of Foreign Studies, Seoul 130-791, Korea
**Department of Chemistry, Brown University, Providence, Rhode Island 01912, U.S.A.*
(Received November 18, 1987)

요 약. 암모늄 파라-메칠벤젠슬폰네이트($C_7H_{11}NO_3S$)의 결정 및 분자구조를 실온에서 X-선회절방법으로 결정하였으며 이 화합물의 결정은 사방정계인 $P_{na}2_1$에 속하며 a=20.406(4), b=6.271(1), c=7.067(2)Å, V=904.19Å^3, Z=4, D_x=1.39, D_m=1.38g·cm^{-3}, λ(*Mo Kα*)=0.71069Å, μ=3.1cm^{-1}, T=298*K*, F(000)=400이다. 구조결정은 직접법을 이용하여 풀어 최소자승법으로 정밀화하였다. 최종 R값은 994개의 $I>1\sigma(I)$인 값에 대하여 0.057이다. 메칠벤젠과 황원자는 거의 같은 평면에 있고 SO_3와 암모늄이온간에는 3개의 수소결합으로 연결되어 있다. 그중 둘은 음이온을 c 축방향으로, 나머지 하나는 b축방향으로 연결하여 2차원적인 친수성분자층을 형성한다. 이들 분자층간에는 메칠벤젠기들이 모여있어 소수성분자층을 형성하고 있다.

ABSTRACT. Ammonium *p*-methylbenzenesulfonate, $C_7H_{11}NO_3S$, Mr=189.23, orthorhombic, space group $Pna2_1$, a=20.406(4), b=6.271(1), c=7.067(2)Å, V=904.19Å^3, Z=4, Dx=1.39, Dm=1.38g·cm^{-3}, λ(*Mo Kα*)=0.71069Å, μ=3.1cm^{-1}, T=298*K*, F(000)=400, final R=0.057 for 994 unique observed reflections with $I>16\sigma(I)$. The methylbenzene portion including the sulfur atom is nearly planar. Between the SO_3 groups and the ammonium ion, there are three unique hydrogen bonds; two of which make the anions linked along the *c*-axis and the remaining one along the *b*-axis. These hydrogen bonds make two-dimensionally hydrogen-bonded molecular layers. Among these hydrophilic layers, the methylbenzene moieties cluster together to form hydrophobic layers.

INTRODUCTION

Alkylbenzenesulfonic acids in the form of salts have both polar ionic and non-polar hydrophobic moieties. They form micelles in the aqueous solution so that the hydrocarbon moieties cluster together. In effort to determine the crystal packing modes of the salts of alkylbenzenesulfonic acids, single crystal *x*-ray analysis of ammonium *p*-methylbenzenesulfonate has been undertaken.

EXPERIMENTAL

A transparent crystal of ammonium *p*-methylbenzenesulfonate (AMBS), 0.2×0.3×0.4mm, was obtained by slow evaporation of a equimolar mixture of ammonium hydroxide and *p*-methylbenezenesulfonic acid at room temperature. The density was measured by floatation method in CCl_4/benzene. Preliminary oscillation and Weissenberg photographs were used to determine cell parameters and space group. Accurate cell dimensions were obtained by a least squares refinement of 2θ angles for 25 reflections ($25<2\theta<35°$). Data collections were carried out at room temperature using Nicolet R3m diffractometer with graphite-monochromated *Mo Kα* radiation. The intensities of 1131 reflections were collected by *a* $\theta-2\theta$ scan technique at variable rates of 4.9~29.3 min^{-1} with $2\theta_{max}=55°$ for the ranges $0\leqslant h\leqslant 26$, $0\leqslant k\leqslant 8$, $0\leqslant 1\leqslant 9$; three reflections monitored every 97 reflections with no decrese in intensity over the course of data collection, 994 unique observed reflections with $I>1\sigma(I)$ used for refinement. The structure was solved by direct methods, all hydrogen atoms found on difference map; for refinement the C—H and the N—H bond lengths fixed at 0.96Å and 0.93Å respectively and the methyl and the ammonium groups refined as rigid group with ideal geometry; anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic parameters for hydrogen atoms (20% greater than that of attached atoms). Refinement of 128 parameters carried out by cascade block-diagonal least squares on *F* with maximum(sin $\theta)/\lambda=0.46Å^{-1}$, converged at $R=0.057$, $wR=0.062$; $w=1/(\sigma^2(F)+0.00114F^2)$ where $\sigma^2(F)$ is from statistics of counting; goodness of fit=1.161; $(\Delta/\sigma)_{max}=-0.04$ in final cycle; highest peak in final difference map 0.28, lotwest hole -0.25 $eÅ^{-3}$. Atomic scatering factors[1] were taken from International Tables for X-ray Crvstallography(1974). No corrections for absorption were made. All calculations were perfomed on a Data General Eclips S140 computer using the SHELXTL 5.1 program package[2] (Nicolet Instrument Company, 1984).

Table 1. Atom coordinates ($\times10^4$) and temperature factors ($Å^2\times10^3$)

atom	*x*	*y*	*z*	*U*
C(1)	678(2)	1899(6)	6979(9)	35(1)*
C(2)	504(2)	3899(7)	7595(8)	44(1)*
C(3)	−152(2)	4484(8)	7638(9)	47(2)*
C(4)	−637(2)	3086(7)	7073(9)	40(1)*
C(5)	−450(2)	1103(8)	6381(8)	45(2)*
C(6)	200(2)	494(7)	6331(7)	39(1)*
C(7)	−1343(2)	3732(10)	7112(17)	69(2)*
N	2464(2)	1007(5)	1879(16)	48(1)*
O(1)	1815(3)	2202(10)	8514(7)	70(2)*
O(2)	1788(3)	1993(13)	5207(8)	92(3)*
O(3)	1528(2)	−1106(5)	6990(19)	97(2)*
S	1509(1)	1151(2)	6883(2)	42(1)*
Hna	2208(19)	1297(58)	2932(47)	26
Hnb	2205(26)	958(95)	806(54)	63
Hnc	2774(15)	2089(45)	1755(80)	67
Hnd	2679(18)	−285(40)	2055(82)	83
H(2)	836(2)	4889(7)	7995(8)	48
H(3)	−271(2)	5885(8)	8065(9)	51
H(5)	−779(2)	136(8)	5931(8)	49
H(6)	321(2)	884(7)	5853(8)	44
H(7a)	1380(2)	5122(10)	7665(17)	75
H(7b)	−1590(2)	2719(10)	7838(17)	75
H(7c)	−1504(2)	3761(10)	5836(17)	75

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalised *U* tensor.

DISCUSSION

Atomic coordinates and equivalent isotropic thermal parameters are listed in *Table* 1. Bond lengths and bond angles are listed in *Table* 2 and 3. A thermalellipsoid plot of the molecule with the atomic numbering scheme is presented in *Fig.* 1. The *p*-methylbenzene ring is nearly planar; the mean plane of seven atoms C(1)

Table 2. Bond lengths (Å)

C(1)—C(2)	1.375(6)	C(1)—C(6)	1.392(6)
C(1)—S	1.760(4)	C(2)—C(3)	1.390(7)
C(3)—C(4)	1.380(7)	C(4)—C(5)	1.389(7)
C(4)—C(7)	1.496(6)	C(5)—C(6)	1.380(6)
O(1)—S	1.467(5)	O(2)—S	1.416(6)
O(3)—S	1.418(3)		

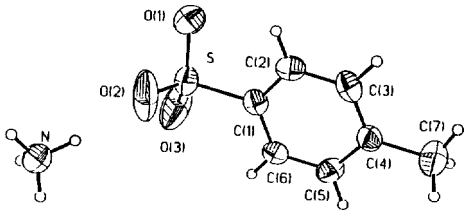

Fig. 1. Molecule of AMBS showing the atomic numbering scheme and thermal ellipsoids.

through C(7) is given by the equation:

$$-1.573x-2.294y+6.554z=4.0119$$

and the maximum deviation from this plane is 0.019Å for C(1). The sulfur atom is also coplanar with the deviation of −0.002Å from this plane.

Bond lengths and bond angles for the methylbenzene ring are all within normal ranges[3,4]. Tetrahedral angles around the sulfur atom show variations from the ideal value, ranging from −4.5 to +3.8°. The S—O bond lengths are in the range 1.416(6)−1.467(5)Å, of which the S—O(1)=1.467(5)Å is longer than others. Within the accuracy of the experimental structural results, these agree with the reported data of the S—O bond lengths(Murray-Rust & Glen, 1982 and Joswig & Fuess, 1982[4,5]). Selected torsion angles are listed in *Table* 4.

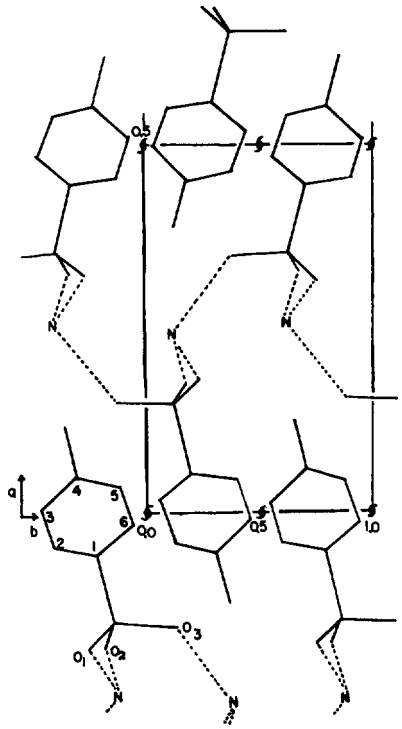

Fig. 2. Projection of the structure along the *c*-axis. (Dotted lines indicate hydrogen bonds).

The views of the crystal packing along the *c*-and *b*-axes are given in *Fig.* 2 and *Fig.* 3, in which the hydrogen bonding scheme is also indicated As shown in the figures, each ammonium ion forms three N—H···O hydrogen bonds with three *p*-methylbenzenesulfonate ions; of which N—H···O(1) (2.824Å) and N—H···O(2) (2.795Å) make the anions linked along the *c*-

Table 3. Bond angles (deg.)

C(2)—C(1)—C(6)	120.0(4)	O(2)—C(1)—S	120.3(3)
C(6)—C(1)—S	119.6(3)	C(1)—C(2)—C(3)	119.8(4)
C(2)—C(3)—C(4)	121.1(4)	C(3)—C(4)—C(5)	118.2(4)
C(3)—C(4)—C(7)	120.8(5)	C(5)—C(4)—C(7)	120.9(4)
C(4)—C(5)—C(6)	121.4(4)	C(1)—(6)—C(5)	119.3(4)
C(1)—S—O(1)	105.0(3)	C(1)—S—O(2)	108.7(3)
O(1)—S—O(2)	108.6(4)	C(1)—S—O(3)	106.9(2)
O(1)—S—O(3)	113.3(5)	O(2)—S—O(3)	114.0(6)

Table 4. Selected torsion angles (deg.)

C(2)—C(1)—S—O(1)	35.4(6)	C(6)—C(1)—S—O(1)	−148.1(5)
C(2)—C(1)—S—O(2)	−80.6(6)	C(6)—C(1)—S—O(2)	95.9(6)
C(2)—C(1)—S—O(3)	156.0(7)	C(6)—C(1)—S—O(3)	−27.5(8)

Table 5. Hydrogen bonds in ammonium *p*-methylbenzenesulfonate

bond	position of A	H···A	D···A	∠D—H···A
N-Hna-O(2)	x, y, z	1.87Å	2.795Å	173°
N-Hnb-O(1)	$x, y, z-1$	1.97	2.824	153
N-Hnc-O(3)	$1/2-x$, $1/2+y$, $-1/2+z$	1.83	2.741	166

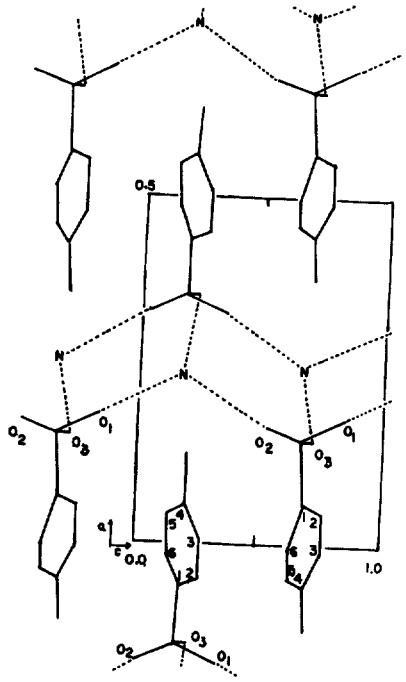

Fig. 3. Projection of the structure along the *b*-axis.

axis and the remaining N—H···O(3) (2.741Å) along the *b*-axis. These hydrogen bonds make two-dimensionally hydrogen-bonded molecular layers. Between these hydrophilic molecular layers, the methylbenzene moieties cluster together forming a hydrophobic layer nearly parallel to the *bc* plane. Geometrical details of the hydrogen bonds are given in *Table* 5. There are only van der Waals interaction within the hydrophobic layers and the shortest contact is 3.679Å between carbon atoms.

인 용 문 헌

1. International Tables for X-ray Crystallography (1974). Vol. 1V, Birmingham: Kynoch Press.
2. Sheldrick, G.M. (1985). SHELXTL Crystallographic System, Version 5.1 Nicolet XRD Corporation, Madison, Wisconsin.
3. G. Germain and J.P. Declercq, *Acta Cryst.*, **C39**, 230 (1983).
4. P. Murray-Rutsand R.C. Glen, *Acta Cryst.*, **B38**, 2696 (1982).
5. W. Joswig and H. Fuess, *Acta Cryst.*, **B38**, 2798 (1982).