Instrumental Achievements

— X-Ray Analysis —

Crystal Structure of Arsenazo I

Michio ZENKI*, Takashi SHIBAHARA*, Mikio YAMASAKI* and Yoshihiko KUSHI**

*Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama 700, Japan

**College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Arsenazo I (Neothorin), 3-[(2-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid has been known as a sensitive reagent for Th, Zr and alkaline earth metals.^{1,2} Our main interest lies in the reactions of mono- or bisaryazo chromotropic acid derivatives with various metal ions. As a part of serial studies, an X-ray analysis of Arsenazo I has been undertaken.

A red-orange needle crystal (0.34×0.19×0.12 mm), grown from 2 M HCl solution, was used for the X-ray study. As shown in Fig. 2, the molecule is very nearly planar. The distances, OH1-OH2, OH1-N1, OH1-OA2 and N1-OA2 were 2.55(2), 2.57(2), 2.85(2) and 3.05(1) Å, respectively; it can be assumed that three intramolecular hydrogen bondings exist as indicated in Fig. 1. The abnormally short distances SB2-OSB are due to the large thermal vibrations. All of the waters of crystallization were disordered (Table 2). The structure of metal chelates with this reagent will be reported elsewhere.

Table 1 Crystal and experimental data

Formula: C ₁₆ H ₁₃ N ₂ O ₁₁ S ₂ As·3H ₂ O	
Formula weight=602.34	
Crystal system: triclinic	
Space group: $P\bar{1}$	Z=2
$a=14.880(6)$ Å	$\alpha=89.01(3)^\circ$
$b=12.245(4)$ Å	$\beta=99.63(3)^\circ$
$c=7.338(3)$ Å	$\gamma=101.54(3)^\circ$
$V=1291.4(8)$ Å ³	
$D_x=1.549$ g/cm ³	
$R=0.071$	
No. of reflections used=2570	
Measurement: Rigaku AFC-6A	
Program system: UNICS II	
Structure determination: heavy atom method	
Refinement: block-diagonal least-squares

Fig. 1 Chemical structure.

Fig. 2 A perspective view with atom numbering.

Table 2 Final coordinates of non-H atoms

	x	y	z	$B_{eq}/\text{\AA}^2$
AS	0.1108(1)	1.3665(1)	0.2894(2)	2.67(3)
SA1	-0.0701(2)	0.7487(2)	0.2259(4)	2.3(1)
OA1	0.1192(7)	1.4608(6)	0.115(1)	4.2(3)
OA2	0.2010(5)	1.3026(6)	0.318(1)	3.2(2)
OA3	0.1189(6)	1.4607(5)	0.463(1)	3.6(3)
OSA1	-0.1076(5)	0.7812(6)	0.379(1)	2.9(2)
OSA2	-0.0764(5)	0.6247(5)	0.222(1)	3.1(2)
OSA3	-0.1101(5)	0.7845(6)	0.045(1)	3.1(2)
OH1	0.2130(6)	1.0728(6)	0.324(2)	5.4(3)
OH2	0.3797(6)	1.0413(7)	0.388(2)	8.7(5)
N1	0.0434(6)	1.0984(6)	0.269(1)	2.6(3)
N2	0.0190(6)	0.9869(7)	0.258(1)	2.5(3)
CA1	-0.0290(8)	1.1550(8)	0.244(2)	2.5(3)
CA2	-0.1226(8)	1.102(1)	0.209(2)	3.7(4)
CA3	-0.1928(9)	1.164(1)	0.184(2)	4.4(4)
CA4	-0.169(1)	1.281(1)	0.188(2)	5.1(5)
CA5	-0.0792(8)	1.3335(9)	0.221(2)	3.4(4)
CA6	-0.0112(8)	1.2733(8)	0.247(2)	2.8(3)
CB1	0.0826(7)	0.9249(8)	0.277(2)	2.3(3)
CB2	0.1810(8)	0.9691(8)	0.312(2)	3.2(4)
CB3	0.2466(8)	0.8929(8)	0.336(2)	3.1(4)
CB4	0.3413(8)	0.9315(9)	0.376(3)	5.3(5)
CB5	0.403(1)	0.861(1)	0.407(3)	7.2(7)
CB6	0.365(1)	0.743(1)	0.386(3)	6.5(6)
CB7	0.2696(8)	0.700(1)	0.349(2)	4.7(5)
CB8	0.2113(8)	0.7774(8)	0.322(2)	3.1(4)
CB9	0.1091(8)	0.7338(9)	0.282(2)	3.2(4)
CB10	0.0477(8)	0.8045(7)	0.263(2)	2.4(3)
SB2	0.4424(3)	0.6511(4)	0.424(1)	11.1(3)
OSB1	0.489(2)	0.669(1)	0.272(5)	27.(2)
OSB2	0.3916(8)	0.5463(9)	0.412(3)	13.1(8)
OSB3	0.509(1)	0.692(1)	0.565(5)	26.(2)
OW1A	0.690(3)	0.797(3)	0.328(6)	8.(1) ^a
OW1B	0.690(1)	0.700(2)	0.385(3)	9.7(5) ^a
OW2A	0.700(2)	0.769(3)	-0.042(5)	9.3(9) ^a
OW2B	0.717(2)	0.850(2)	0.112(4)	11.8(8) ^a
OW3A	0.627(3)	0.585(4)	-0.147(8)	16.(2) ^a
OW3B	0.675(2)	0.668(2)	-0.152(5)	14.0(9) ^a

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i a_j$$

a. Isotropic temperature factors were applied. The following occupancy factors were used for the disordered atoms: OW1A, 0.3; OW1B, 0.7; OW2A, 0.4; OW2B, 0.6; OW3A, 0.4; OW3B, 0.6.

Table 3 Bond distances ($\text{\AA}$) and angles ($^\circ$)

AS—OA1	1.713(8)	CA4—CA5	1.345(18)
AS—OA2	1.667(8)	CA5—CA6	1.353(18)
AS—OA3	1.705(8)	CB1—CB2	1.437(15)
AS—CA6	1.921(11)	CB1—CB10	1.461(13)
SA1—OSA1	1.434(9)	CB2—CB3	1.468(17)
SA1—OSA2	1.502(7)	CB3—CB4	1.377(16)
SA1—OSA3	1.461(8)	CB3—CB8	1.406(14)
SA1—CB10	1.727(11)	CB4—CB5	1.375(20)
OH1—CB2	1.263(12)	CB5—CB6	1.442(18)
OH2—CB4	1.350(13)	CB6—CB7	1.392(18)
N1—N2	1.341(11)	CB6—SB2	1.750(16)
N1—CA1	1.380(15)	CB7—CB8	1.396(18)
N2—CB1	1.316(15)	CB8—CB9	1.488(16)
CA1—CA2	1.398(15)	CB9—CB10	1.369(17)
CA1—CA6	1.419(13)	SB2—OSB1	1.394(37)
CA2—CA3	1.399(19)	SB2—OSB2	1.348(11)
CA3—CA4	1.402(18)	SB2—OSB3	1.337(25)

OA1—AS—OA2	110.2(4)	OH1—CB2—CB1	121.5(10)
OA1—AS—OA3	96.7(4)	OH1—CB2—CB3	118.7(10)
OA1—AS—CA6	108.8(4)	CB1—CB2—CB3	119.8(9)
OA2—AS—OA3	112.1(4)	CB2—CB3—CB4	121.8(9)
OA2—AS—CA6	117.0(4)	CB2—CB3—CB8	118.8(10)
OA3—AS—CA6	110.1(5)	CB4—CB3—CB8	119.3(11)
N2—N1—CA1	115.8(8)	OH2—CB4—CB3	122.2(11)
N1—N2—CB1	120.8(8)	OH2—CB4—CB5	115.6(11)
N1—CA1—CA2	123.2(9)	CB3—CB4—CB5	122.2(11)
N1—CA1—CA6	120.6(9)	CB4—CB5—CB6	117.2(12)
CA2—CA1—CA6	116.1(11)	CB5—CB6—CB7	122.3(14)
CA1—CA2—CA3	120.4(11)	CB5—CB6—SB2	118.0(11)
CA2—CA3—CA4	119.5(12)	CB7—CB6—SB2	119.6(10)
CA3—CA4—CA5	120.9(14)	CB6—CB7—CB8	117.1(11)
CA4—CA5—CA6	119.6(11)	CB3—CB8—CB7	121.8(10)
AS—CA6—CA1	124.4(9)	CB3—CB8—CB9	120.3(10)
AS—CA6—CA5	112.1(7)	CB7—CB8—CB9	117.9(9)
CA1—CA6—CA5	123.4(10)	CB8—CB9—CB10	121.0(9)
N2—CB1—CB2	123.9(9)	SA1—CB10—CB1	121.3(9)
N2—CB1—CB10	115.9(9)	SA1—CB10—CB9	118.9(7)
CB2—CB1—CB10	120.2(10)	CB1—CB10—CB9	119.8(10)

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