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The Crystal Structure of 1-(2-Thiazolylazo)-6-bromo-2-naphthol

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The crystals of 1-(2-thiazolylazo)-6-bromo-2-naphthol are orthorhombic, with a space group of $P2_12_12_1$, and with unit-cell dimensions of $a=19.044(3)$, $b=31.996(9)$, $c=4.221(1)$ Å, and $z=8$. The crystal structure was solved by the heavy-atom method and refined by the least-squares technique to give an R value of 0.064 for 1608 observed reflections. Both of the two crystallographically independent molecules show a generally similar shape and size. The phenolic oxygen atom is linked to the azo nitrogen atom adjacent to the thiazole ring by intramolecular hydrogen bonding, the O···N distances being 2.54 Å.

1-(2-Thiazolylazo)-2-naphthol(hereafter abbreviated as H-TAN) is a useful analytical reagent for metals. The crystal structures of H-TAN[1] and its metal chelates[2-5] have been determined in order to elucidate the structural change on chelate-ring formation; however, it is possible that the observed conformation for H-TAN is affected by the packing forces. Accordingly, it was desirable to determine the structures of several H-TAN derivatives. The title compound (H-TANBr shown in Fig. 1) was selected. A preliminary communication of this work based on the photographic data has been reported.[6] We will now present a refined structure of H-TANBr based on the newly collected diffractometer data.

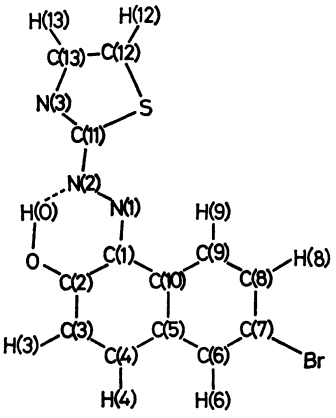

Fig. 1. Numbering of atoms.

Experimental

Red needle crystals of H-TANBr were grown by the sublimation of crude materials. The crystal data are summarized in Table 1. Both the determination of the cell constants and the collection of the intensity data were carried out on a Rigaku automatic four-circle diffractometer, using Cu$K\alpha$ radiation monochromatized with a graphite plate. The density was measured by floatation in an aqueous solution of sodium iodide.

Table 1. Crystal data

$C_{13}H_8N_3OSBr$	$V=2572.2$Å^3
F. W.$=334.2$	$Z=8$
Orthorhombic	$D_m=1.72$ g·cm^{-3}
Space group: $P2_12_12_1$	$D_x=1.72$ g·cm^{-3}
$a=19.044(3)$Å	$\mu=61.9$ cm^{-1} (for Cu$K\alpha$)
$b=31.996(9)$Å	
$c=$ 4.221(1)Å	

Using the ω-2θ scan technique at a scan rate of 4 °/min, the integrated intensities were measured up to $2\theta=120$ °. The scan ranges were determined according to this formula: $1.5° + 0.6° \times \tan\theta$. The background counts were taken on both sides of each peak for 10 s. The net counts were corrected for Lorentz and polarization effects; no absorption correction was made. The intensities of three standard reflections measured at every 50 reflections showed no significant variations during data collection. From this data set, 1608 reflections with $F \geq 3\sigma(F)$ were used for the subsequent calculations.

Structure Determination and Refinement

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method on the basis of a set of photographic data ($hk0 \sim hk3$ and $0kl$).[6] The R value was 0.12 for 2074 reflections ($R=0.105$ for 1570 non-zero reflections).

Refinement was continued using the data collected on the diffractometer. Anisotropic thermal parameters were employed for the bromine and sulfur atoms, R being reduced to 0.086. A difference synthesis calculated at this stage did not show any significant hydrogen peaks. The hydrogen atoms attached to the ring systems, whose positions were assumed from the suitable geometry and B's to be 5.5 Å^2, were included in the structure-factor calculations in subsequent refinements, but they were not refined. The final R value was 0.064 for the 1608 observed reflections. A unit weight was given to each reflection. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[7] The least-squares calculations were performed using the HBLS-4 program.[8] The final coordinates and thermal parameters are given in Table 2. The observed and calculated structure amplitudes are listed in Table 3.***

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*** Table 3 is kept as Document No. 7611 at the Chemical Society of Japan, 1-5, Kanda, Surugadai, Chiyoda-ku, Tokyo 101.

Table 2. Atomic parameters and their e.s.d.'s[a)]

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	y/c	B
Br	0.6621(1)	0.5604(1)	−0.6985(5)		C(12)	0.3249(8)	0.3702(4)	0.5852(43)	4.7(3)
Br′	0.2727(1)	0.2239(1)	0.0949(6)		C(13)	0.3450(8)	0.3311(4)	0.5919(42)	4.6(3)
S	0.3811(2)	0.4001(1)	0.3579(12)		O′	0.6920(5)	0.1654(3)	−0.0488(30)	5.3(3)
S′	0.5596(2)	0.5132(1)	−0.7121(12)		N(1′)	0.5743(6)	0.1235(3)	−0.3261(33)	3.8(2)
O	0.5809(5)	0.3155(3)	−0.2267(28)	4.4(2)	N(2′)	0.6368(6)	0.1087(3)	−0.3873(33)	4.1(3)
N(1)	0.5058(6)	0.3898(3)	−0.0167(29)	3.4(2)	N(3′)	0.6937(6)	0.0533(4)	−0.6548(36)	5.0(3)
N(2)	0.4870(6)	0.3541(3)	0.0867(32)	3.7(2)	C(1′)	0.5692(7)	0.1571(4)	−0.1407(39)	3.5(3)
N(3)	0.4046(6)	0.3212(4)	0.4145(36)	4.7(3)	C(2′)	0.6278(8)	0.1792(5)	−0.0021(43)	4.8(4)
C(1)	0.5631(6)	0.3896(4)	−0.2209(36)	3.1(3)	C(3′)	0.6150(9)	0.2144(5)	0.1854(51)	6.2(4)
C(2)	0.6001(7)	0.3532(4)	−0.3190(41)	3.9(3)	C(4′)	0.5487(8)	0.2295(5)	0.2358(46)	5.2(4)
C(3)	0.6585(8)	0.3575(4)	−0.5236(40)	4.4(3)	C(5′)	0.4888(7)	0.2088(4)	0.0924(42)	4.3(3)
C(4)	0.6794(7)	0.3960(4)	−0.6255(42)	4.4(3)	C(6′)	0.4207(7)	0.2246(4)	0.1563(42)	4.4(3)
C(5)	0.6437(7)	0.4330(4)	−0.5393(36)	3.7(3)	C(7′)	0.3655(7)	0.2027(4)	0.0123(41)	4.3(3)
C(6)	0.6674(7)	0.4716(4)	−0.6411(38)	3.7(3)	C(8′)	0.3725(8)	0.1676(4)	−0.1559(44)	4.7(3)
C(7)	0.6334(7)	0.5072(4)	−0.5515(40)	4.0(3)	C(9′)	0.4398(7)	0.1521(4)	−0.2088(40)	3.8(3)
C(8)	0.5751(6)	0.5057(4)	−0.3459(38)	3.4(3)	C(10′)	0.4995(7)	0.1723(4)	−0.0846(39)	3.6(3)
C(9)	0.5505(7)	0.4675(4)	−0.2398(39)	3.5(3)	C(11′)	0.6372(7)	0.0745(4)	−0.5723(39)	3.8(3)
C(10)	0.5852(6)	0.4299(4)	−0.3298(36)	3.0(3)	C(12′)	0.6084(8)	0.0132(5)	−0.8888(46)	5.2(4)
C(11)	0.4274(7)	0.3548(4)	0.2855(43)	4.1(3)	C(13′)	0.6764(8)	0.0188(5)	−0.8333(47)	5.4(4)

Anisotropic temperature factors[b)] ($\times 10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	30(1)	11(1)	699(12)	−6(1)	−10(5)	15(3)
Br′	45(1)	14(1)	983(18)	15(1)	79(7)	9(4)
S	33(1)	10(1)	741(34)	5(1)	−22(13)	−29(7)
S′	24(1)	10(1)	755(33)	−1(1)	−17(12)	14(7)

a) E.s.d.'s in parentheses are in units of least significant digit. b) The anisotropic temperature factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

	x/a	y/b	z/c		x/a	y/b	z/c
H(3)	0.6845	0.3313	−0.5961	H(3′)	0.6575	0.2280	0.3036
H(4)	0.7235	0.3983	−0.7646	H(4′)	0.5416	0.2561	0.3713
H(6)	0.7116	0.4742	−0.7791	H(6′)	0.4129	0.2505	0.3051
H(8)	0.5516	0.5331	−0.2775	H(8′)	0.3290	0.1526	−0.2497
H(9)	0.5082	0.4665	−0.0853	H(9′)	0.4473	0.1252	−0.3470
H(12)	0.2820	0.3815	0.7076	H(12′)	0.5862	−0.0112	−0.0179
H(13)	0.3173	0.3082	0.7089	H(13′)	0.7141	−0.0011	−0.9210

Description of the Structures and Discussion

The structure consists of two crystallographically independent H-TANBr molecules (referred to as A and B). Figure 2 shows their conformations projected on the naphthalene plane. As can be seen in the figure, the A and B molecules show generally similar shapes. Each azo group adopts a *trans* conformation, and the oxygen atom is linked to the azo nitrogen atom adjacent to the thiazole ring by intramolecular hydrogen bonding, the O···N(2) distances being 2.54 Å.

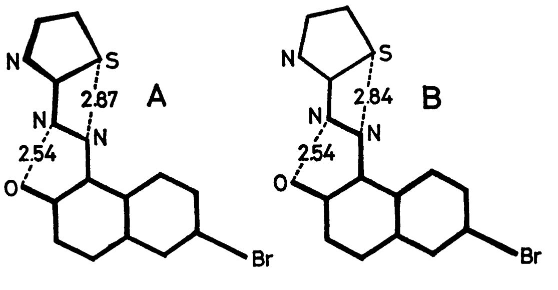

Fig. 2. Conformation of H-TANBr molecules. Views are perpendicular to the naphthalene plane.

Molecules A and B are nearly planar, with maximum deviations of 0.15 and 0.07 Å respectively. The A molecule is twisted along the N(1)–C(1) bond, and the naphthol ring makes an angle of 6.7° with the thiazole ring, whereas the B molecule is slightly folded at N(2), and the angle between the thiazole and naphthol rings is 1°. Similar features were observed in the crystals of H-TAN.[1)]

It seems that there is no definite reason to restrict the rotation around the C(11)–N(2) bond. In all four crystallographically independent molecules, two in noncentrosymmetric H-TANBr crystals and two in centrosymmetric H-TAN crystals, however, N(1) and N(3) are in the *trans* position. This indicates that the observed conformation is the most stable one. There is no evidence for the strong intermolecular interaction which dominates the molecular conformation. Short intramolecular non-bonded distances of 2.87 Å in A and 2.84 Å in B are found between S and N(1) (Fig. 2).

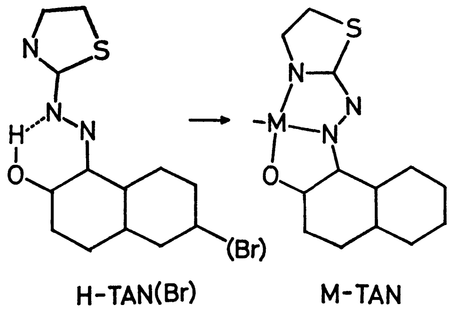

Fig. 3. A comparison of the structures between H-TAN(Br) and M-TAN.

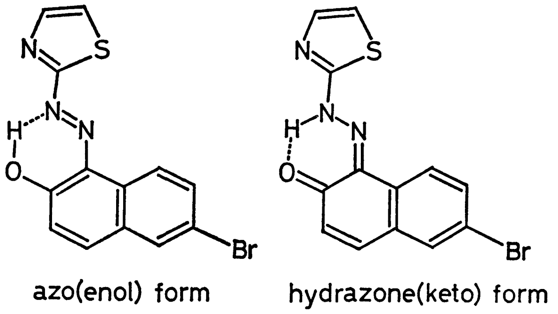

Fig. 4. Two possible tautomers for H-TANBr.

Figure 3 compares the structures of H-TAN(Br) and its metal chelate(M-TAN). If, in solution, the H-TAN(Br) molecules exist in the same conformation as in a solid, it is apparent that both of the two ring systems attached to the central azo group are rotated by 180° upon chelate-ring formation.

The bond lengths and angles are shown in Table 4, along with their estimated standard deviations. All the distances except for that of C(7)-Br agree with the values observed in the crystal of H-TAN, within the range of experimental error. The coexistance of azo and hydrazone tautomers in the crystalline state of H-TAN has been reported[1] previously on the basis of the difference in the electron density map and the examination of the relevant bond lengths. The good agreement in the distances of N(1)–N(2), C(2)–O between H-TANBr and H-TAN may, therefore, indicate that, in the present crystal also, there are the azo and hydrazone tautomers shown in Fig. 4.

The crystal structure projected along the c-axis is shown in Fig. 5. Intermolecular distances less than 3.5 Å are given in Table 5. The molecular planes of both A and B are inclined by about 45° from the (001) plane. This stacking scheme of the molecules along the c-axis is very similar to that of H-TAN. The molecular arrangements in the ab-plane, however, differ considerably from each other as a result of the large effective volume of bromine atoms.

TABLE 4. BOND LENGTHS AND ANGLES WITH e.s.d.'s IN PARENTHESES

	A	B		A	B
Bond lengths (Å)					
S-C(11)	1.72(2)	1.76(2)	C(3)-C(4)	1.36(2)	1.37(3)
S-C(12)	1.73(2)	1.71(2)	C(4)-C(5)	1.41(2)	1.45(3)
O-C(2)	1.32(2)	1.31(2)	C(5)-C(6)	1.38(2)	1.42(3)
N(1)-N(2)	1.28(2)	1.31(2)	C(5)-C(10)	1.43(2)	1.40(2)
N(1)-C(1)	1.39(2)	1.33(2)	C(6)-C(7)	1.36(2)	1.40(3)
N(2)-C(11)	1.41(2)	1.35(2)	C(7)-C(8)	1.41(2)	1.34(3)
N(3)-C(11)	1.28(2)	1.32(2)	C(8)-C(9)	1.38(2)	1.39(3)
N(3)-C(13)	1.40(2)	1.38(3)	C(9)-C(10)	1.42(2)	1.41(2)
C(1)-C(2)	1.42(3)	1.45(2)	C(12)-C(13)	1.31(3)	1.33(3)
C(1)-C(10)	1.43(2)	1.43(3)	Br-C(7)	1.89(2)	1.93(2)
C(2)-C(3)	1.42(2)	1.40(3)			
Bond angles (°)					
C(11)-S-C(12)	87(1)	89(1)	C(5)-C(6)-C(7)	120(2)	115(2)
N(2)-N(1)-C(1)	115(1)	118(1)	C(6)-C(7)-C(8)	121(2)	125(2)
N(1)-N(2)-C(11)	114(1)	114(1)	C(6)-C(7)-Br	117(1)	116(1)
C(11)-N(3)-C(13)	108(2)	111(2)	C(8)-C(7)-Br	122(1)	119(1)
N(1)-C(1)-C(2)	125(1)	125(2)	C(7)-C(8)-C(9)	120(2)	118(2)
N(1)-C(1)-C(10)	115(1)	116(1)	C(8)-C(9)-C(10)	120(1)	121(2)
C(2)-C(1)-C(10)	120(1)	119(1)	C(1)-C(10)-C(5)	119(1)	120(2)
O-C(2)-C(1)	122(2)	120(2)	C(1)-C(10)-C(9)	123(1)	122(2)
O-C(2)-C(3)	119(2)	121(2)	C(5)-C(10)-C(9)	118(1)	117(2)
C(1)-C(2)-C(3)	119(2)	119(2)	S-C(11)-N(2)	122(1)	122(1)
C(2)-C(3)-C(4)	121(2)	122(2)	S-C(11)-N(3)	117(1)	112(1)
C(3)-C(4)-C(5)	122(2)	120(2)	N(2)-C(11)-N(3)	121(2)	125(2)
C(4)-C(5)-C(6)	121(1)	119(2)	S-C(12)-C(13)	111(1)	111(2)
C(4)-C(5)-C(10)	119(1)	119(2)	N(3)-C(13)-C(12)	116(2)	116(2)
C(6)-C(5)-C(10)	121(1)	122(2)			

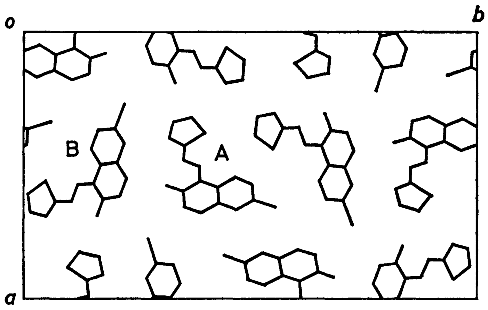

Fig. 5. The crystal structure projected along the c-axis.

Calculations were carried out on a FACOM 270-30 computer at the Computer Center of Osaka City University, and on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

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TABLE 5. INTERMOLECULAR DISTANCES LESS THAN 3.5Å

		Symmetry operation	Distance (Å)
S	C(12)	2	3.48
O	C(4′)	1	3.41
N(1)	C(11)	2	3.48
N(2)	N(3)	2	3.40
N(2)	C(1)	3	3.45
N(2)	C(2)	3	3.25
N(3)	C(6′)	1	3.32
C(6)	C(9)	2	3.36
C(1)	C(4)	3	3.33
C(11)	C(13)	2	3.38
C(12)	O′	4	3.13
C(13)	O′	4	3.27
S′	N(1′)	2	3.45

Symmetry operations
1 (x y z) 3 (x y $1+z$)
2 (x y $-1+z$) 4 ($\frac{1}{2}+x$ $\frac{1}{2}-y$ $1+z$)

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