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## Crystal and Molecular Structure of 2-Thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole

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2-Thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole crystallizes as the monohydrate ( $C_{12}H_{14}N_2O_4S \cdot H_2O$ ) in the orthorhombic space group  $P2_12_12_1$  with  $a = 21.726$  (8),  $b = 9.006$  (3), and  $c = 6.875$  (2) Å,  $Z = 4$ . The structure has been determined from 1194 X-ray intensities measured on a Picker four-circle automated diffractometer with Cu  $K\alpha$  radiation. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final  $R$  of 0.04. The nucleoside adopts the *syn* conformation with a glycosyl torsion angle  $\chi_{CN}$  of  $249.8^\circ$ , and the mode of puckering of the ribose ring is  $C(2')\text{-endo-C}(1')\text{-exo}$  ( ${}^2T_1$ ). These conformational features are consistent with the other known 8-substituted purine nucleosides. The conformation about the  $C(4')\text{-C}(5')$  bond is *gauche-trans*. All potential sites on the sugar and base are involved in hydrogen bonding and the sulfur atom is found to accept two hydrogen bonds, one from the water molecule and the other from an adjacent  $O(5')$  hydroxyl group. There is no interbase hydrogen bonding. The bases form a stacked column along alternating screw axes running parallel to  $c$ . The interplanar base separation is 3.42 Å and the shortest interbase contact is 3.61 Å involving the  $C(4)$  and  $C(8)$  atoms of adjacent bases. The stacking pattern observed here differs markedly from those reported for the 8-halogenated nucleosides as well as the majority of the known thio purine crystal structures.

### Introduction

2-Thio-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole (TRB) belongs to a class of nucleoside analogs containing a benzimidazole base. The compound could exist in one of two tautomeric structures shown in Fig. 1. The benzimidazole base is also of biological interest since 5,6-dimethyl-1-( $\alpha$ -D-ribofuranosyl)-benzimidazole occurs as a fragment of vitamin  $B_{12}$ . The purpose of this study was to obtain information on the molecular dimensions and conformation and to compare it with the structure of the 2-chloro-1-( $\beta$ -D-ribofuranosyl)-benzimidazole (CRB) which was recently completed in this laboratory (Sprang & Sundaralingam, 1973). In addition

it was of interest to determine the effects of the thio substituent on the base stacking, the hydrogen bonding and the overall conformation of the structure and to compare them with other sulfur-containing nucleic acid base analogs.

### Experimental

A crystal with dimensions approximately 0.2 mm in all directions was chosen for the X-ray structure analysis. The crystal was mounted about  $c$ . The systematic absences:  $h00, h = 2n + 1$ ;  $0k0, k = 2n + 1$ ;  $00l, l = 2n + 1$ , show that the crystal belongs to the space group  $P2_12_12_1$ . The cell constants were determined from a least-squares refinement of the  $2\theta$ ,  $\omega$  and  $\chi$  angles of 12 medium-angle reflections measured on our Picker

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FACS-1 automated diffractometer and were found to be  $a=21.726$  (8),  $b=9.006$  (3) and  $c=6.875$  (2) Å. The density determined by the method of flotation in a  $\text{CCl}_4$  and cyclohexane mixture was  $1.421 \text{ g cm}^{-3}$  and compares favorably with the calculated density of  $1.422 \text{ g cm}^{-3}$  assuming four molecules of the monohydrate in the unit cell. Complete three-dimensional intensity data up to  $2\theta=127^\circ$  were collected on the diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation, the  $\theta$ - $2\theta$  scan technique being employed. The standard deviation of an intensity  $\sigma(I)$  was computed from counting statistics and an electronic instability factor of 0.02 (Stout & Jensen, 1968). Of the 1304 scanned reflections 1194 had  $I > 1.5\sigma(I)$  and were corrected for the usual Lorentz and polarization factors and used in the structure analysis.

### Structure determination

The solution was obtained in a straightforward manner by Patterson techniques in conjunction with direct methods. The sulfur atom was located unambiguously

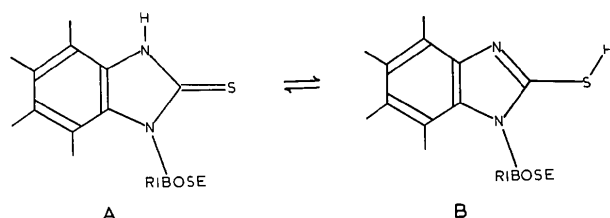


Fig. 1. The two tautomeric forms of 2-thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole.

from the Harker sections and the phases of 184 reflections with  $|E| > 1.4$  were refined by the tangent formula to a Karle & Karle  $R$  of 0.20 with the X-RAY 70 programs (Stewart, Kundell & Baldwin, 1970). The  $E$  map generated with these phases revealed the entire structure including the water molecule among the 21 strongest peaks in the map.

### Structure refinement

The positional and thermal parameters of the 20 non-hydrogen atoms were refined with the full-matrix least-squares program of Busing, Martin & Levy (1962) modified for use on the Univac 1108 computer by Rao (1968). Four cycles of isotropic refinement lowered  $R$  to 0.09. Two further cycles of anisotropic refinement reduced  $R$  to 0.07. The 16 hydrogen atoms were located in a difference synthesis and were included in the subsequent refinement cycles of the nonhydrogen atoms. The hydrogen atoms were fixed with the temperature factor of the atoms to which they were attached. At this point the data were corrected for secondary extinction (Zachariasen, 1963) and the nonhydrogen atoms were subjected to two additional cycles of anisotropic refinement which gave a final  $R$  of 0.040 for the 1194 reflections. The ratios of the shifts to the estimated standard deviations in the parameters were all considerably less than unity with a maximum of 0.30.

A Hughes type weighting scheme was applied in the refinement where  $1/\sqrt{w} = 0.034|F_o| + 2.0$  for  $|F_o| > 80$  and  $1/\sqrt{w} = 4.75$  for  $|F_o| \leq 80$ . The scattering factors used for S, O, N and C atoms were those of Cromer & Waber (1965) while that of H was from Stewart, Davidson & Simpson (1965).

Table 1. Positional and thermal parameters of atoms in 2-thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole

Positional parameters of nonhydrogen atoms have been multiplied by  $10^4$ .

Positional parameters of hydrogen atoms have been multiplied by  $10^3$ .

Anisotropic thermal parameters have been multiplied by  $10^4$ .

Anisotropic temperature factor is of the form  $\exp[-\beta_{11} \times h^2 + \dots + 2\beta_{12} \times hk + \dots]$ .

Standard deviations refer to the least significant digits.

	$x$	$y$	$z$	$\beta_{11}$ or $B$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	1309 (0)	893 (1)	-210 (2)	20 (1)	54 (1)	202 (3)	-1 (1)	-23 (1)	4 (2)
N(1)	1450 (1)	3934 (4)	-498 (5)	14 (1)	59 (4)	133 (8)	0 (1)	-4 (2)	2 (5)
C(2)	1691 (2)	2520 (5)	-461 (6)	15 (1)	67 (5)	105 (9)	5 (1)	-7 (2)	-5 (6)
N(3)	2305 (2)	2675 (4)	-579 (5)	14 (1)	88 (4)	146 (9)	4 (1)	-2 (2)	-8 (6)
C(4)	3048 (2)	4822 (6)	-644 (7)	14 (1)	141 (4)	139 (11)	-3 (2)	-2 (3)	4 (8)
C(5)	3054 (2)	6352 (6)	-608 (8)	16 (1)	152 (8)	159 (12)	-17 (2)	8 (3)	4 (8)
C(6)	2515 (2)	7184 (6)	-528 (7)	19 (1)	109 (6)	160 (11)	-11 (2)	1 (3)	5 (7)
C(7)	1941 (2)	6506 (5)	-476 (8)	17 (1)	83 (5)	155 (11)	-4 (1)	3 (3)	-12 (7)
C(8)	1932 (2)	4972 (5)	-539 (6)	13 (1)	84 (5)	90 (9)	-2 (1)	3 (2)	-2 (6)
C(9)	2471 (2)	4166 (5)	-600 (6)	15 (1)	101 (5)	102 (9)	-2 (2)	3 (2)	-4 (7)
C(1')	796 (2)	4247 (5)	-359 (6)	14 (1)	48 (4)	129 (9)	2 (1)	0 (2)	-2 (6)
O(1')	691 (1)	4915 (3)	1461 (4)	16 (1)	75 (3)	103 (6)	10 (1)	-4 (1)	3 (4)
C(2')	539 (2)	5321 (5)	-1841 (6)	17 (1)	61 (5)	107 (9)	-3 (1)	-4 (2)	-6 (5)
O(2')	412 (1)	4573 (3)	-3622 (4)	26 (1)	91 (4)	116 (7)	-3 (1)	-14 (2)	3 (4)
C(3')	-31 (2)	5917 (5)	-800 (6)	15 (1)	66 (5)	141 (10)	5 (2)	-9 (2)	1 (6)
O(3')	-550 (1)	4948 (4)	-1029 (5)	15 (1)	121 (4)	181 (7)	-6 (1)	-16 (1)	25 (5)
C(4')	161 (2)	5878 (5)	1328 (6)	13 (1)	65 (4)	129 (9)	6 (2)	-2 (2)	19 (6)
C(5')	319 (2)	7379 (5)	2151 (7)	23 (1)	72 (5)	138 (10)	5 (2)	-5 (2)	-3 (6)
O(5')	491 (1)	7165 (3)	4125 (5)	28 (1)	86 (4)	144 (7)	3 (1)	-16 (2)	-16 (4)
O(W)	3255 (2)	578 (5)	-1044 (7)	25 (1)	155 (6)	347 (12)	19 (1)	-10 (2)	-64 (7)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$ or <i>B</i>
H(3)	262	198	-30	2.8
H(4)	345	438	-41	3.0
H(5)	348	687	-43	3.4
H(6)	255	849	-65	3.2
H(7)	152	725	-38	3.1
H(1')	62	326	-42	1.9
H(2')	86	613	-207	2.5
H(O2')	45	519	-449	3.2
H(3')	-14	698	-130	2.5
H(O3')	-76	548	-216	3.1
H(4')	-19	546	224	2.1
H(51)	64	778	146	2.8
H(52)	-7	793	198	2.8
H(O5')	55	802	479	3.2
H(W1)	362	32	-29	4.0
H(W2)	326	-3	-248	4.0

## Results

The atomic parameters are listed in Table 1 and the observed and calculated structure amplitudes in Table 2. The thermal ellipsoids (Johnson, 1965) of the atoms are shown in Fig. 2. The bond distances and angles are shown in Fig. 3, while the molecular packing, hydrogen bonding and base stacking schemes are illustrated in Figs. 4-7.

## Discussion

### The tautomeric structure of the base

The base was found to exist in the thio form (*A*) (Fig. 1) with N(3) protonated rather than the alternative tautomeric structure (*B*). In this regard TRB resembles the other known sulfur analogs of the nucleic acid bases, all of which occur in the thio form (Lin, Sundaralingam & Arora, 1971).

### Geometry of the benzimidazole base

The carbon-carbon bond lengths in the benzene portion of the base are equal within experimental error. This however is not the case with the endocyclic angles. The angles at C(5), C(6), C(8) and C(9) are equal within experimental error and average  $121.8^\circ$  while the angles at C(4) and C(7) are also equal but their average value of  $116.3^\circ$  is  $5.5^\circ$  smaller than the other angles in the ring. Similar results were obtained in CRB (Sprang & Sundaralingam, 1973). Unlike CRB the observed tautomeric structure in TRB possesses an exocyclic double bond (C=S). This markedly alters the geometry of the imidazole portion of the base compared with CRB and the normal purine nucleosides. The N(3)-C(2) bond in TRB has more single-bond character than the corresponding N(7)-C(8) bond in the normal purine nucleosides. Similarly the C(8)-N(1) bond length is longer than the corresponding C(4)-N(9) bond in the purine nucleosides. The endocyclic bond angles show considerable variations between TRB and the purine nucleosides. The C-S bond length,  $1.693 \text{ \AA}$ , is in good agreement with those found for other thio purine and pyrimidine structures (Lin *et al.*, 1971). The glycosyl bond

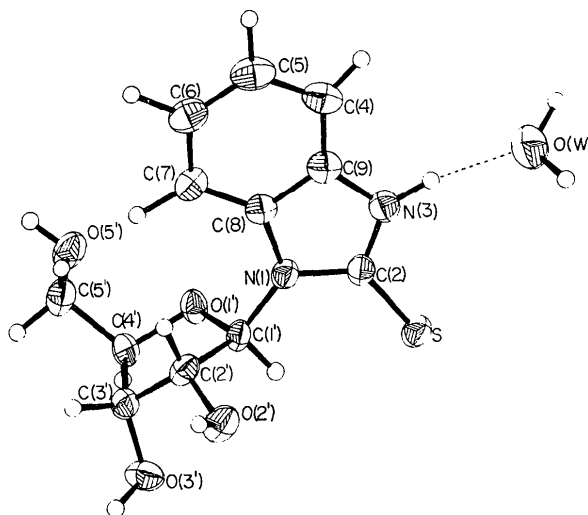


Fig. 2. The ellipsoids of thermal vibrations of the nonhydrogen atoms.

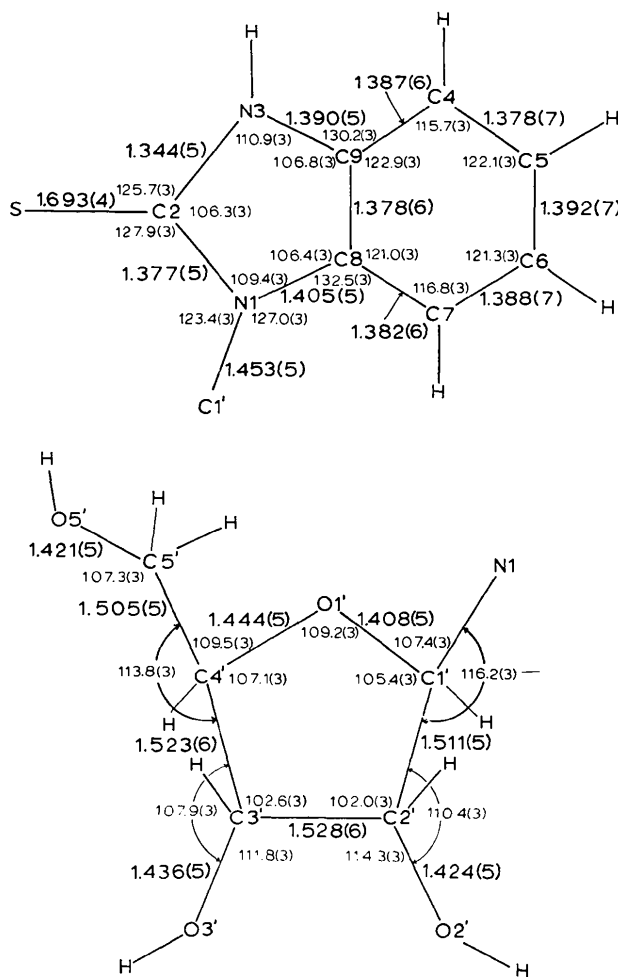


Fig. 3. The bond lengths and bond angles involving the nonhydrogen atoms.

distance, 1.453 Å, is also consistent with the purine nucleosides in the *syn* conformation (Rao & Sundaralingam, 1970).

*Deviations from planarity of the base*

Table 3 shows the deviations of the atoms from the least-squares planes through the base atoms. The at-

oms of the benzene ring lie in a plane, while the atoms of the imidazole ring show somewhat larger deviations. C(2) of the imidazole ring displays the largest deviation while N(1) and C(8) show the next largest displacements. The dihedral angle between the five- and six-membered rings is 1.9°. The sulfur atom is markedly displaced on the same side as the ring atom C(2).

Table 2. Observed and calculated structure amplitudes ( $\times 10$ ) for 2-thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole

h k l	2 214 290	0 465 302	410 0	7 226 226	2 404 433	8 77	78 12 261	246	7 238 268	12 151 151	0 776 800	...
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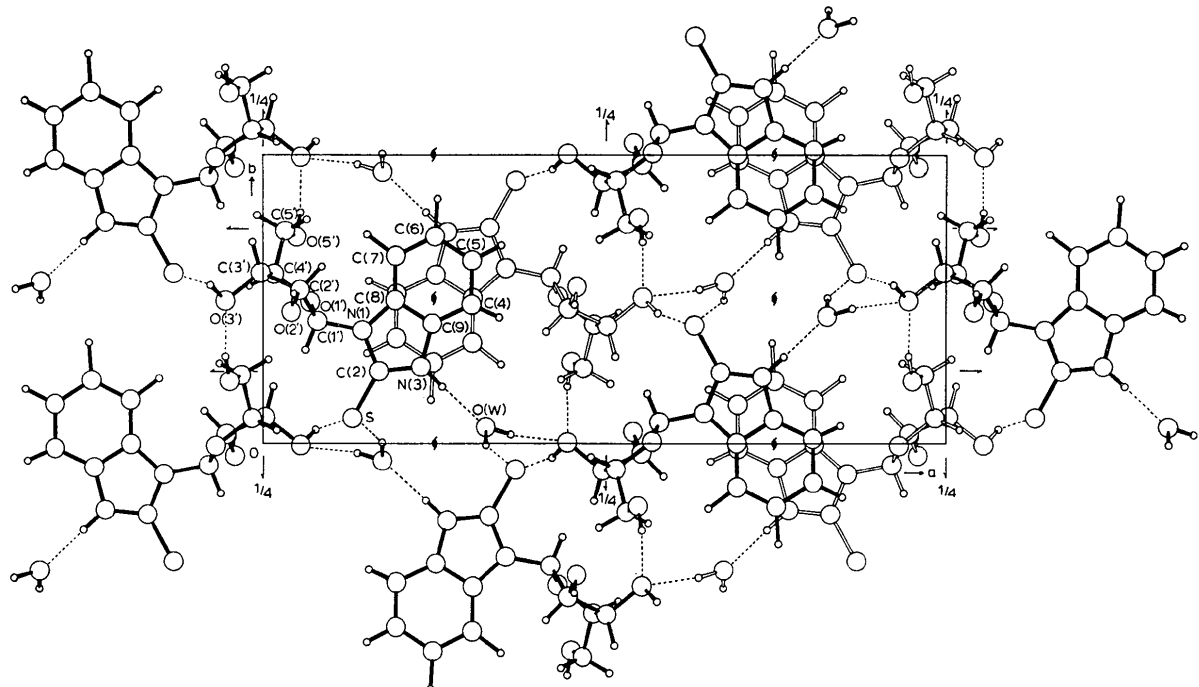


Fig. 4. A view along c showing the hydrogen bonding and the base stacking.

Table 3. Deviations ( $\text{\AA}$ ) of the atoms from the least-squares plane for the base

Atoms used in fitting the least-squares planes are denoted by asterisks.

Atom	Plane I	Plane II	Plane III
S	0.191	0.141	0.252
N(1)	-0.021*	-0.015*	0.006
C(2)	0.035*	0.017*	0.075
N(3)	-0.000*	-0.012*	0.035
C(4)	-0.006*	0.027	0.002*
C(5)	0.005*	0.067	0.003*
C(6)	0.012*	0.086	-0.002
C(7)	0.010*	0.067	0.007*
C(8)	-0.021*	0.008*	0.008*
C(9)	-0.015*	0.002*	0.004*
C(1')	0.022	0.029	0.049
r.m.s. deviation of fitted atoms	0.017	0.012	0.005

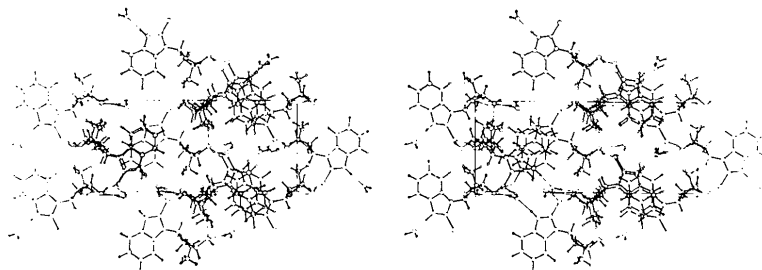
### The sugar

The bond angles and distances of the ribose moiety compare favorably with those usually found in nucleosides and nucleotides having C(2')-endo pucker (Sundaralingam & Jensen, 1965; Sundaralingam, 1973). The largest variation between the endocyclic and exocyclic angles are associated with the atom C(2') which shows the greatest puckering.

The bond distances and bond angles involving hydrogen atoms are within the normal range and are summarized in Table 4.

Table 4. Bond distances and angles involving hydrogen atoms

	Range	Mean
C-H bonds	0.97-1.13 $\text{\AA}$	1.02 $\text{\AA}$
N-H bonds		0.94
O-H bonds		0.96
C-C-H angle (tetrahedral)	103-114 $^\circ$	109 $^\circ$
O-C-H angle (tetrahedral)	109-112	111
C-O-H angle (tetrahedral)	99-113	106
C-C-H angle	113-129	120
C-N-H angle	117-129	123
H-C-H angle (tetrahedral)		113
H-O-H angle		109

Fig. 6. A stereoscopic view of the molecular packing along *c*.

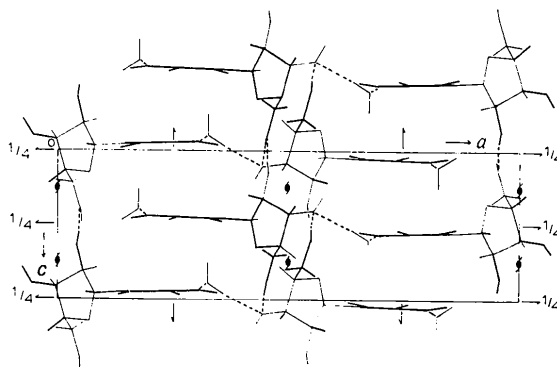
### Molecular conformation

The mode of puckering of the ribose is C(2')-endo-C(1')-exo ( ${}^2T_1$ ) (Sundaralingam, 1965; 1972). The ring torsion angles and the pseudorotation parameters  $P$  (phase angle) and  $\tau_{\max}$  (maximum amplitude of puckering) for the ribose ring are shown in Table 5. These values are similar to those found for CRB and lie within the normal range found for the  $\beta$ -nucleosides (Altona & Sundaralingam, 1972).

Table 5. Torsional angles in 2-thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole

Glycosyl angle	$\chi$	-110.2 $^\circ$
Sugar ring torsion angles	$\tau^0$	-27.3
	$\tau_1$	36.9
	$\tau_2$	-31.9
	$\tau_3$	17.0
Phase angle of pseudorotation	$P$	152.1
	Maximum amplitude of pseudorotation	$\tau_{\max}$
Sugar puckering		C(2')-endo-C(1')-exo( ${}^2T_1$ )
Conformation about C(4')-C(5')		<i>gauche-trans</i>

TRB exhibits a glycosyl torsion angle [O(1')-C(1')-N(1)-C(2)] of 249.8 $^\circ$ , which falls within the *syn* range (Donohue & Trueblood, 1960; Sundaralingam, 1969).

Fig. 5. A view along *b* showing the base stacking and the alternating hydrophobic and hydrophilic regions.

It has already been established that bulky substituents such as bromine or chlorine in the 8-position of purine nucleosides would tend to exclude the *anti* conformation (Tavale & Sobell, 1970; Bugg & Thewalt, 1969; Sprang & Sundaralingam, 1973). Similarly the 2-thio (position 8 in purine numbering) substituent excludes the *anti* conformation in TRB. We were especially interested to know whether the *syn* conformation promoted by the above steric interactions between the sulfur and the ribose CH<sub>2</sub>OH group would destabilize the *gauche-gauche* conformation about the C(4')-C(5') bond by virtue of any possible steric interaction between H(7) of the base and the O(5') atom of the sugar. In fact it appeared to us at first that the observed *gauche-trans* (Table 5) conformation in TRB was a result of the latter interaction. But our later studies on CRB showed that the *gg* conformation is allowed even when the benzimidazole base assumes the *syn* conformation (Sprang & Sundaralingam, 1973). There are no intramolecular contacts less than the sum of the van der Waals radii.

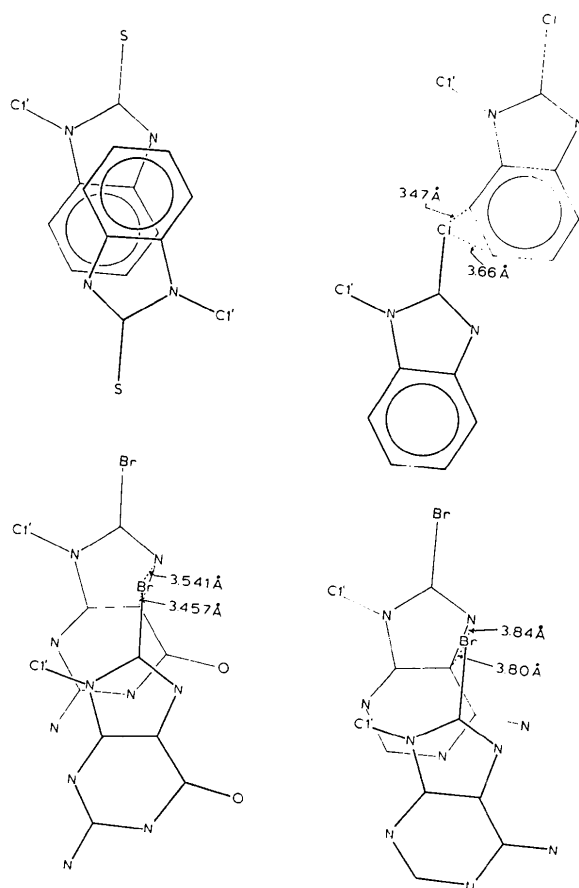


Fig. 7. A view normal to the base of 2-thio-1-( $\beta$ -D-ribofuranosyl)-3H-benzimidazole (TRB), 2-Cl-1-( $\beta$ -D-ribofuranosyl)benzimidazole (CRB), 8-Br-guanosine, and 8-Br-adenosine showing the stacking patterns.

### Hydrogen bonding and crystal packing

The hydrogen bonding and base stacking are shown in Figs. 4 and 5, which are projections along *c* and *b*, respectively. The hydrogen bond distances and angles are given in Table 6.

All potential sites on the ribose and the base are involved in hydrogen bonding. The sulfur accepts two hydrogen bonds, one from O(3') [O(3') $\cdots$ S=3.180 Å] and the other from the water [O(W) $\cdots$ S=2.998 Å]. The O(W) $\cdots$ S hydrogen-bond distance of 2.998 Å is the shortest found so far amongst the thio nucleosides. The importance of sulfur hydrogen bonding in the crystal structures of thio purines and thio pyrimidines has been amply illustrated by Thewalt & Bugg (1972) and Lin *et al.* (1971). The former workers note that of the 15 structures studied there were only two in which sulfur did not accept at least one hydrogen bond. There is no base-base hydrogen bonding in this structure.

The molecular packing consists of alternating zones of stacked bases and ribose moieties (Figs. 5 and 6). The benzimidazole rings are stacked in a head-to-tail fashion and show a considerable degree of overlap with an interplanar separation of 3.42 Å. In TRB the sulfur atom points away from adjacent bases and is exposed to the water in contrast to the majority of the known thio nucleoside crystal structures where the sulfur substituent makes close contacts with an adjacent ring while the rings themselves do not show great overlap (Thewalt & Bugg, 1972). The observed stacking is also in marked contrast to that observed for CRB, 8-Br-adenosine, and 8-Br-guanosine where the halogen atoms are involved in halogen-base interactions (Bugg, Thomas, Sundaralingam & Rao, 1971; Sprang & Sundaralingam, 1973). A comparison of the base stacking patterns and the shorter contacts in these compounds is shown in Fig. 7.

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Table 6. *Hydrogen-bond lengths and angles*  
 Estimated standard deviations are given in parentheses.

Symmetry operation	Translation			Atoms	Angle ( $^{\circ}$ )	Length ( $\text{\AA}$ )	Length from hydrogen ( $\text{\AA}$ )
	X	Y	Z				
(1)	0	0	0	N(3)—H(3)·····O(W)	153	2·816 (5)	1·94
(1)	0	0	+1	O(2')—H(O2')···O(5')	160	2·806 (5)	2·02
(2)	0	0	0	O(3')—H(O3')···S	162	3·180 (5)	2·18
(2)	0	0	-1	O(5')—H(O5')···O(3')	170	2·831 (5)	1·93
(3)	0	0	0	O(W)—H(W2)···S	155	2·998 (5)	2·23
(4)	0	0	0	O(W)—H(W1)···O(3')	170	3·295 (5)	3·02

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

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## Structure Cristalline du Sulfure de Thallium: $Tl_4S_3$

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The crystal structure of  $Tl_4S_3$  has been determined by X-ray diffraction methods. The space group is  $P2_1/a$  and the cell constants are  $a=7.97$ ,  $b=7.76$ ,  $c=13.03$  Å,  $\gamma=103.99^{\circ}$ . The structure was solved by the heavy-atom method and refined by a least-squares program to a final  $R$  value of 0.08. One trivalent thallium atom is in tetrahedral coordination and forms isolated linkages with the three other  $Tl^+$  which appear to be by electrostatic interaction.

L'existence vraisemblable d'un composé  $Tl_4S_3$  a été signalée par Hahn & Klingler (1949). Plus récemment, d'après Soulard & Tournoux (1971), il est apparu que le composé  $Tl_4S_3$  puisse être dimorphe: la forme  $\beta$  se transformerait en forme  $\alpha$  par broyage, mais la transformation inverse n'a pu être obtenue. Par l'étude d'un monocristal de  $Tl_4S_3$   $\beta$ , ces auteurs ont mis en évidence un réseau monoclinique et un groupe spatial identiques à ceux que nous observons, mais la structure n'a pas été étudiée.

Kabré (1972), en reprenant l'étude des sulfures de thallium, a isolé des monocristaux de  $Tl_4S_3$  qui ont servi à l'étude de la structure. Ils ont été préparés en mettant en présence du thallium et du soufre en quan-

tité stoechiométrique et sous vide. Le mélange a été porté à une température de  $600^{\circ}\text{C}$ , maintenu pendant 48 h, puis refroidi très lentement jusqu'à la température ambiante avec un palier de 2 semaines à  $180^{\circ}\text{C}$ .  $Tl_4S_3$  a une température de fusion non congruente de  $274^{\circ}\text{C}$ .

### Données expérimentales

Les cristaux de  $Tl_4S_3$  ont la forme de plaquettes allongées suivant la direction [100] et sont de couleur noire avec des reflets métalliques.

La symétrie de la maille est monoclinique et les paramètres mesurés sur clichés de Weissenberg et affinés sur 12 raies du cliché de poudre sont: