Crystal Structure of *N*-(*p*-Bromophenylcarbamoyl)thiamine Anhydride (N,S-*cis*-Type)

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The crystal structure of the title compound has been determined by three-dimensional *X*-ray analysis. The crystals are monoclinic, $a = 8{\cdot}736$, $b = 11{\cdot}668$, $c = 20{\cdot}451$ Å, $\beta = 99° 21'$, $Z = 4$, space group $P2_1/c$. The structure was solved from diffractometer data by Patterson, Fourier, and refined by least-squares methods, to R 0·065 for 2583 independent observed reflections. The overall shape of the molecule was closely similar to that found in the N,S-*trans*-type molecule, but the configuration of the thiacyclobutane ring is significantly twisted, in contrast with the planar N,S-*trans* type. The thiacyclobutane ring is slightly puckered with a dihedral angle of *ca.* 175°.

In 1968 Takamizawa and Sakai[1] reported a new synthesis of thiamine anhydride (see Scheme) and identified the two stereoisomers, (I) and (II). In conjunction with a chemical study[2-4] of thiamine anhydride, we have recently determined the structure of the *N*-(*p*-bromophenylcarbamoyl) derivative (Ia) (N,S-*trans* type).[5] We now describe the crystal structure of the isomer (IIa) (N,S-*cis* type), and compare the molecular conformations of the *cis*- and *trans*-isomers.

EXPERIMENTAL

Crystals of (IIa) were prepared and recrystallized from chloroform as colourless prisms, m.p. 206—208 °C, elongated along the *b* axis. Precession and Weissenberg photographs were taken with Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation; space group and unit-cell dimensions were determined from the precession photographs and on the automatic diffractometer.

Crystal Data.—$C_{19}H_{20}BrO_2N_5S$, $M = 462{\cdot}4$, Monoclinic, $a = 8{\cdot}736 \pm 0{\cdot}002$, $b = 11{\cdot}668 \pm 0{\cdot}003$, $c = 20{\cdot}451 \pm 0{\cdot}004$, $\beta = 99°21' \pm 2'$, $U = 2057$ Å^3, $D_m = 1{\cdot}463$ (by flotation), $Z = 4$, $D_c = 1{\cdot}492$, $F(000) = 944$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $h0l$, when l is odd, $0k0$ when k is odd. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 22·42 cm^{-1}.

The three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle diffractometer Y 290 controlled by a PDP 8 computer. Integrated intensities were measured for $\theta \leqslant 27{\cdot}5°$ by the θ—2θ scan technique by use of Mo-K_α radiation and a scintillation counter (with a zirconium filter and pulse-height analyser). Each reflection was integrated in 80 steps of intervals of 0·01°. In this way 4730 independent reflections were recorded, of which 3242 were considered to be sufficiently above background and were used in the subsequent analysis. All the intensities were corrected for Lorentz and polarization factors, and the structure amplitudes were derived. No absorption corrections were applied since the specimen was considered to be sufficiently small (0·30 × 0·35 × 0·43 mm).

Structure Analysis.—The position of the bromine atom was determined from three Harker sections of the three-dimensional Patterson synthesis as $x = 0{\cdot}390$, $y = 0{\cdot}105$, $z = 0{\cdot}375$. A first set of structure factors was calculated for 1070 reflections up to $\sin\theta/\lambda = 0{\cdot}40$, and the related three-dimensional Fourier synthesis was summed with phases based on the bromine atom. The initial value of R was 0·57, and the positions of eleven atoms were assigned from this electron-density distribution. The other atom positions were successively derived within four subsequent Fourier refinements, and R was reduced to 0·26, with an overall isotropic temperature factor of 3·5 Å^2. When R was 0·26, several cycles of least-squares refinement with the

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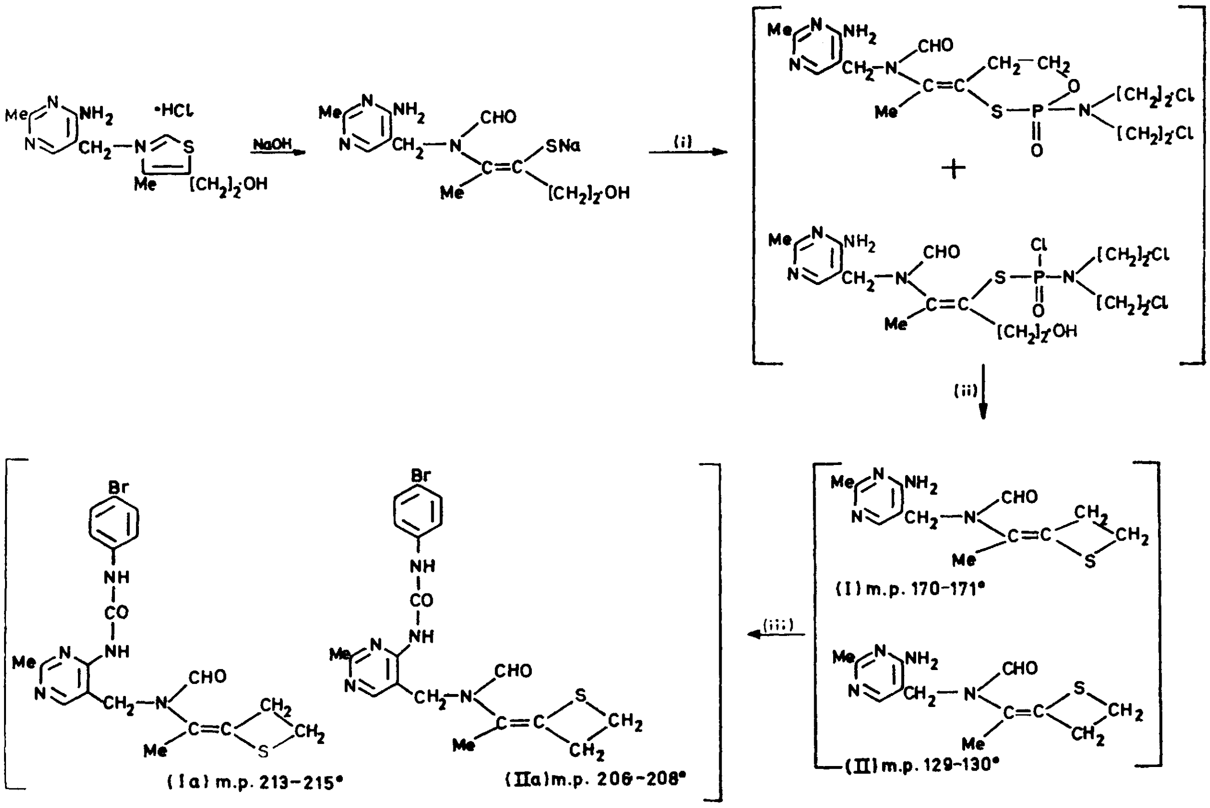

SCHEME

Reagents: i, $\{Cl\cdot[CH_2]_2\}_2N\cdot P(O)Cl_2$ in MeCN; ii, pyridine at 100 °C; iii, p-BrC_6H_4NCO.

TABLE 1

Final fractional atomic co-ordinates and anisotropic thermal parameters,* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·6117(1)	0·8986(1)	0·6256(1)	0·0251(1)	0·0077(1)	0·0040(1)	−0·0005(1)	0·0039(1)	−0·0016(1)
S	0·5310(2)	0·3926(1)	0·2481(1)	0·0167(3)	0·0073(1)	0·0041(1)	0·0019(1)	0·0034(1)	−0·0004(1)
O(1)	0·9225(6)	0·6106(4)	0·3733(2)	0·0191(9)	0·0062(3)	0·0035(1)	−0·0009(4)	0·0032(3)	0·0000(2)
O(2)	0·9920(6)	0·4351(4)	0·2348(2)	0·0172(8)	0·0069(3)	0·0031(1)	−0·0025(4)	0·0015(2)	0·0000(1)
C(3)	0·6743(8)	0·7844(6)	0·5685(3)	0·0153(10)	0·0082(5)	0·0022(1)	0·0005(6)	0·0004(3)	−0·0013(2)
C(4)	0·7554(8)	0·8124(6)	0·5195(3)	0·0149(10)	0·0059(5)	0·0027(1)	−0·0004(5)	0·0010(3)	−0·0000(2)
C(5)	0·8009(8)	0·7295(6)	0·4787(3)	0·0132(10)	0·0078(5)	0·0022(1)	−0·0010(5)	0·0006(3)	0·0000(2)
C(6)	0·7648(8)	0·6165(5)	0·4893(3)	0·0159(10)	0·0052(4)	0·0023(1)	−0·0000(5)	0·0006(3)	0·0000(2)
C(7)	0·6779(10)	0·5894(6)	0·5392(3)	0·0237(15)	0·0061(5)	0·0025(1)	−0·0006(6)	0·0024(4)	0·0000(2)
C(8)	0·6343(10)	0·6730(6)	0·5786(3)	0·0241(15)	0·0077(6)	0·0022(1)	−0·0014(7)	0·0028(4)	−0·0003(2)
N(9)	0·8047(8)	0·5250(5)	0·4526(2)	0·0255(12)	0·0045(3)	0·0022(1)	−0·0003(5)	0·0026(3)	−0·0000(1)
C(10)	0·8789(7)	0·5264(5)	0·3994(3)	0·0119(9)	0·0061(4)	0·0025(1)	−0·0001(5)	0·0004(3)	−0·0002(2)
N(11)	0·9045(6)	0·4190(4)	0·3724(2)	0·0136(8)	0·0056(3)	0·0021(1)	−0·0008(4)	0·0012(2)	−0·0001(1)
C(12)	0·8743(7)	0·3105(5)	0·3928(3)	0·0148(9)	0·0059(4)	0·0018(1)	−0·0002(5)	0·0003(3)	0·0001(2)
C(13)	0·9065(7)	0·2136(5)	0·3553(2)	0·0110(8)	0·0063(4)	0·0017(1)	0·0001(4)	−0·0006(2)	−0·0001(2)
C(14)	0·8796(8)	0·1110(5)	0·3835(3)	0·0155(10)	0·0056(4)	0·0024(1)	−0·0001(5)	0·0005(3)	0·0002(2)
N(15)	0·8248(8)	0·0978(5)	0·4398(2)	0·0236(12)	0·0064(4)	0·0023(1)	−0·0011(6)	0·0005(3)	0·0007(2)
C(16)	0·7933(10)	0·1916(6)	0·4694(3)	0·0233(15)	0·0082(6)	0·0021(1)	−0·0014(7)	0·0017(4)	0·0006(2)
N(17)	0·8123(7)	0·2990(4)	0·4479(2)	0·0207(11)	0·0059(4)	0·0020(1)	−0·0007(5)	0·0010(3)	0·0003(1)
C(18)	0·9682(6)	0·2214(5)	0·2914(3)	0·0087(7)	0·0058(4)	0·0023(1)	−0·0005(4)	−0·0003(2)	−0·0004(2)
N(19)	0·8561(5)	0·2722(3)	0·2389(2)	0·0093(6)	0·0043(3)	0·0015(1)	−0·0007(3)	0·0003(2)	0·0000(1)
C(20)	0·7153(6)	0·2124(4)	0·2135(2)	0·0105(7)	0·0051(3)	0·0012(1)	−0·0001(4)	0·0008(2)	0·0000(1)
C(21)	0·5813(7)	0·2608(5)	0·2169(3)	0·0135(9)	0·0052(4)	0·0022(1)	0·0002(5)	0·0017(3)	0·0002(2)
C(22)	0·3439(12)	0·3356(11)	0·2059(8)	0·0135(15)	0·0155(12)	0·0081(6)	0·0032(11)	0·0002(7)	−0·0010(7)
C(23)	0·4168(8)	0·2254(7)	0·1889(4)	0·0102(9)	0·0094(7)	0·0039(2)	0·0005(6)	0·0005(3)	−0·0002(3)
C(24)	0·7308(17)	0·1855(9)	0·5331(4)	0·0441(29)	0·0102(8)	0·0026(2)	−0·0050(13)	0·0032(7)	0·0009(3)
C(25)	0·8816(7)	0·3730(5)	0·2124(3)	0·0109(8)	0·0062(4)	0·0019(1)	−0·0010(5)	0·0009(2)	−0·0003(2)
C(26)	0·7323(9)	0·0967(6)	0·1846(4)	0·0122(10)	0·0061(4)	0·0034(2)	−0·0003(5)	0·0009(3)	−0·0005(2)

* In the form: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

programme of King[6] reduced R to 0·16. A three-dimensional difference-Fourier synthesis was then calculated and the 20 hydrogen atom positions were found. The final full-matrix refinement, which was performed on a CDC 6600 computer with the programme of Busing and Levy,[7] reduced R to 0·065 for the 2583 reflections (intensities less than twice the standard deviation of the total counts were rejected). At the final stage of refinement a weighting scheme of the type given by Cruickshank was applied,[8] *i.e.*, $w = (a + |F_o| + c|F_o|^2)^{-1}$, where $a = 8{\cdot}8$ and $c = 0{\cdot}0104$. All hydrogen atoms were included in the final refinement calculations with isotropic temperature factors (B values were fixed at 2·04 Å^2).

Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20259 (8 pp., 1 microfiche).* The atomic scattering factors used in all calculations were taken from ref. 9 for the non-hydrogen atoms and from ref. 10 for the hydrogen atoms. The final positional and thermal parameters with their estimated standard deviations are given in Tables 1 and 2. The bond distances and valency angles are given in Table 3, together with their estimated standard deviations computed from the least-squares residuals.

The molecular packing arrangement along the a axis is illustrated in Figure 1. All intermolecular distances were calculated, and the most significant contacts (< 3·60 Å) are given in Table 4.

TABLE 2

Final fractional co-ordinates for the hydrogen atoms with their standard deviations in parentheses

Atom	x/a	y/b	z/c
H(4)	0·780(8)	0·879(6)	0·506(3)
H(5)	0·902(8)	0·745(6)	0·467(3)
H(7)	0·638(8)	0·512(6)	0·547(3)
H(8)	0·574(8)	0·648(6)	0·608(3)
H(9)	0·791(8)	0·456(7)	0·465(3)
H(11)	0·939(8)	0·427(6)	0·337(3)
H(14)	0·893(8)	0·044(7)	0·356(3)
H(18a)	1·064(8)	0·268(6)	0·301(3)
H(18b)	1·017(8)	0·145(6)	0·280(3)
H(22a)	0·294(10)	0·373(6)	0·174(3)
H(22b)	0·264(9)	0·332(6)	0·238(3)
H(23a)	0·388(8)	0·197(6)	0·147(4)
H(23b)	0·368(8)	0·153(6)	0·215(3)
H(24a)	0·639(9)	0·164(7)	0·527(4)
H(24b)	0·790(8)	0·235(6)	0·578(3)
H(24c)	0·772(8)	0·127(6)	0·574(3)
H(25)	0·798(9)	0·391(6)	0·175(3)
H(26a)	0·631(9)	0·077(6)	0·176(3)
H(26b)	0·793(9)	0·099(6)	0·152(3)
H(26c)	0·773(8)	0·042(6)	0·217(3)

DISCUSSION

The configuration of the molecule is illustrated[11] in Figure 2 where each atom is represented as an ellipsoid to conform with the thermal parameters listed in Table 1.

TABLE 3

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond distances

Br–C(3)	1·909(7)	C(13)–C(14)	1·364(9)
S–C(21)	1·749(6)	C(13)–C(18)	1·494(9)
S–C(22)	1·843(11)	C(14)–N(15)	1·326(10)
O(1)–C(10)	1·209(8)	N(15)–C(16)	1·301(10)
O(2)–C(25)	1·232(7)	C(16)–N(17)	1·347(9)
C(3)–C(4)	1·357(10)	C(16)–C(24)	1·493(14)
C(3)–C(8)	1·370(11)	C(18)–N(19)	1·457(7)
C(4)–C(5)	1·376(10)	N(19)–C(20)	1·435(6)
C(5)–C(6)	1·380(9)	N(19)–C(25)	1·328(7)
C(6)–C(7)	1·402(11)	C(20)–C(21)	1·311(8)
C(6)–N(9)	1·382(9)	C(20)–C(26)	1·490(9)
C(7)–C(8)	1·358(11)	C(21)–C(23)	1·514(9)
N(9)–C(10)	1·354(9)	C(22)–C(23)	1·500(16)
C(10)–N(11)	1·401(8)		
N(11)–C(12)	1·372(8)	N(9)–H · · · N(17)	2·639(8)
C(12)–C(13)	1·420(8)	N(11)–H · · · O(2)	3·040(8)
C(12)–N(17)	1·333(9)		

(*b*) Valency angles

C(21)–S–C(22)	76·5(4)	C(13)–C(14)–N(15)	125·4(6)
Br–C(3)–C(4)	121·3(5)	C(14)–N(15)–C(16)	116·0(6)
Br–C(3)–C(8)	117·6(5)	N(15)–C(16)–N(17)	125·7(7)
C(4)–C(3)–C(8)	121·0(7)	N(15)–C(16)–C(24)	120·0(7)
C(3)–C(4)–C(5)	120·9(6)	N(17)–C(16)–C(24)	114·2(7)
C(4)–C(5)–C(6)	118·7(7)	C(12)–N(17)–C(16)	117·2(6)
C(5)–C(6)–C(7)	119·5(6)	C(13)–C(18)–N(19)	112·0(4)
C(5)–C(6)–N(9)	124·6(6)	C(18)–N(19)–C(20)	120·1(4)
C(7)–C(6)–N(9)	115·7(6)	C(18)–N(19)–C(25)	121·5(4)
C(6)–C(7)–C(8)	120·3(7)	C(20)–N(19)–C(25)	118·2(4)
C(3)–C(8)–C(7)	119·2(7)	N(19)–C(20)–C(21)	119·4(5)
C(6)–N(9)–C(10)	128·4(6)	N(19)–C(20)–C(26)	116·6(5)
O(1)–C(10)–N(9)	126·2(6)	C(21)–C(20)–C(26)	123·8(5)
O(1)–C(10)–N(11)	118·1(6)	S–C(21)–C(20)	132·6(4)
N(9)–C(10)–N(11)	115·6(5)	S–C(21)–C(23)	95·6(4)
C(10)–N(11)–C(12)	130·8(6)	C(20)–C(21)–C(23)	131·5(6)
N(11)–C(12)–C(13)	120·4(6)	S–C(22)–C(23)	92·3(6)
N(11)–C(12)–N(17)	118·3(5)	C(21)–C(23)–C(22)	95·2(6)
C(13)–C(12)–N(17)	121·2(5)	O(2)–C(25)–N(19)	122·8(5)
C(12)–C(13)–C(14)	114·0(5)		
C(12)–C(13)–C(18)	123·6(5)	N(9)–H · · · N(17)	145(7)
C(14)–C(13)–C(18)	122·2(5)	N(11)–H · · · O(2)	169(6)

(*c*) Bond distances associated with hydrogen positions

C(4)–H(4)	0·86(8)	C(22)–H(22b)	1·03(8)
C(5)–H(5)	0·97(7)	C(23)–H(23a)	0·90(8)
C(7)–H(7)	0·98(8)	C(23)–H(23b)	1·11(7)
C(8)–H(8)	0·91(8)	C(24)–H(24a)	0·82(8)
N(9)–H(9)	0·85(8)	C(24)–H(24b)	1·14(7)
N(11)–H(11)	0·82(8)	C(24)–H(24c)	1·09(7)
C(14)–H(14)	0·96(8)	C(25)–H(25)	0·97(7)
C(18)–H(18a)	0·99(7)	C(26)–H(26a)	0·90(8)
C(18)–H(18b)	1·02(7)	C(26)–H(26b)	0·91(8)
C(22)–H(22a)	0·84(7)	C(26)–H(26c)	0·95(7)

TABLE 4

Intermolecular distances (< 3·600 Å)

O(1) · · · C(23$^{\text{II}}$)	3·313	C(4) · · · C(13$^{\text{IV}}$)	3·592
O(1) · · · C(26$^{\text{III}}$)	3·419	C(4) · · · C(14$^{\text{IV}}$)	3·583
O(2) · · · C(14$^{\text{III}}$)	3·493	C(5) · · · C(12$^{\text{IV}}$)	3·569
O(2) · · · C(18$^{\text{III}}$)	3·411	C(5) · · · N(17$^{\text{IV}}$)	3·482
O(2) · · · C(22$^{\text{I}}$)	3·426		
O(2) · · · C(26$^{\text{III}}$)	3·282		

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I	$1 + x, y, z$	III	$2 + \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$
II	$1 + \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	IV	$2 + \bar{x}, 1 + \bar{y}, 1 + \bar{z}$

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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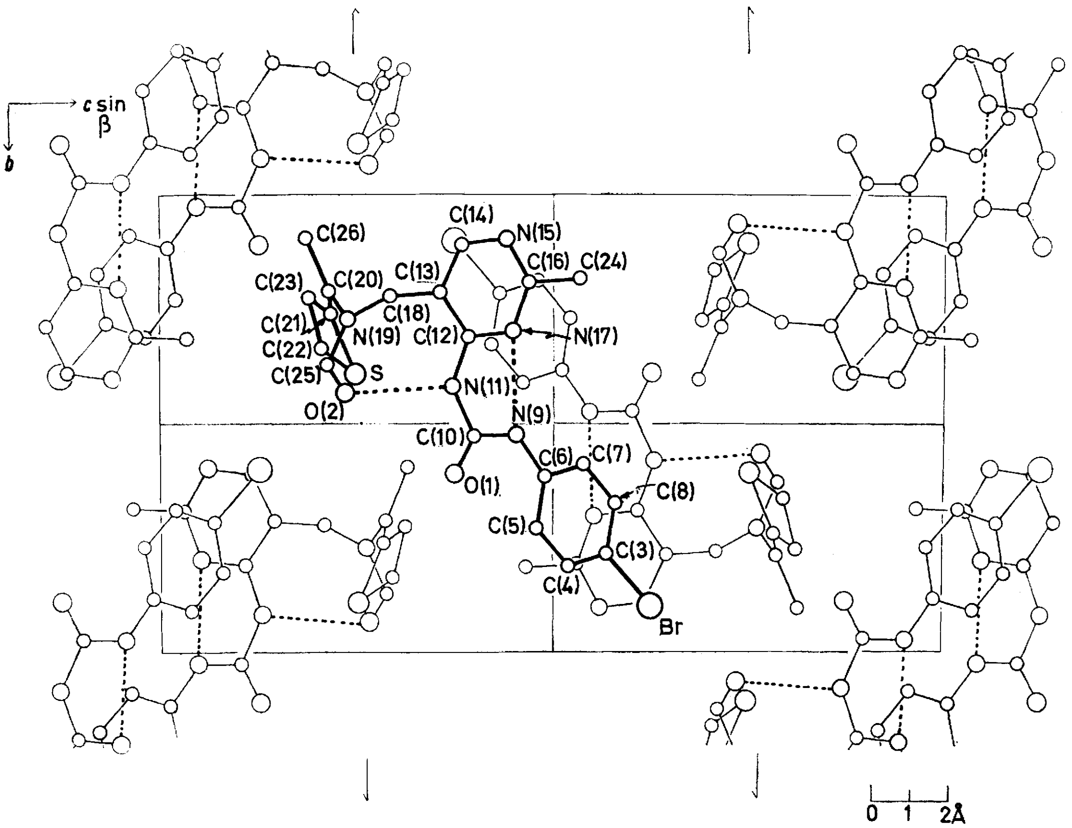

FIGURE 1 The view of the structure looking down *a*

The geometry of the molecule agrees satisfactorily with the results of the structure of *N*-(*p*-bromophenylcarbamoyl)thiamine anhydride (N,S-*trans*), however, a reversal of the configuration (N,S-*cis*) is seen at both sides of the C(20)=C(21) double bond. For the most part the corresponding bond distances and angles are not significantly different from expected values. The value of 1·500 Å found in molecule (IIa) is shorter than a normal C–C bond (1·540 Å) but no satisfactory explanation is possible. The geometry of the pyrimidine ring in the molecules agrees satisfactorily with the geometries of earlier reported thiamine structures.[12-15] The angles at the ring nitrogen atoms in pyrimidines have been given [16] as 114—125°. In order to obtain detailed information on the molecular shape and conformational features, the various dihedral angles and the deviations of atoms from the best plane through the various atom groups were calculated (Tables 5 and 6). Table 6 shows that the benzene ring and the group of atoms N(9), C(10), N(11), and O(1) are planar, but the pyrimidine ring and the thiacyclobutane ring are slightly

TABLE 5

Torsion angles (°) in the molecule

C(10)–N(9)→C(6)–C(5)	−2·6
C(10)–N(9)→C(6)–C(7)	175·5
C(10)–N(11)→C(12)–C(13)	177·8
C(10)–N(11)→C(12)–N(17)	−1·2
C(25)–N(19)→C(18)–C(13)	114·0
C(20)–N(19)→C(18)–C(13)	−67·1
C(21)–C(20)→N(19)–C(25)	−60·1
C(21)–C(20)→N(19)–C(18)	121·0

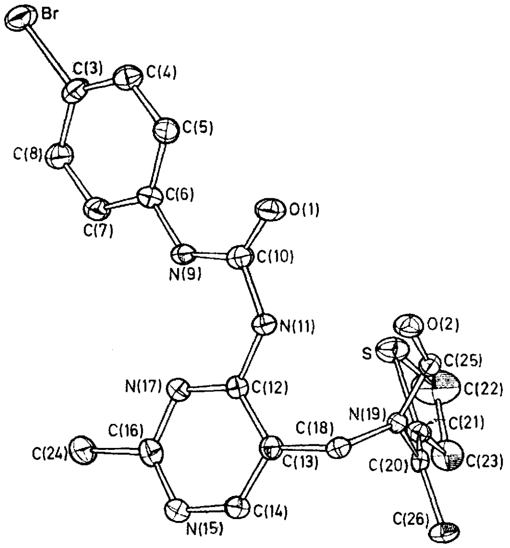

FIGURE 2 A diagram of the molecule

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TABLE 6

Equations of best least-squares planes, and, in square brackets, displacements of the atoms (Å), from the mean planes

Plane (I): C(3)–(8) $0{\cdot}7599X - 0{\cdot}1163Y + 0{\cdot}6395Z' = 9{\cdot}3063$ *

[C(3) 0·00, C(4) 0·00, C(5) 0·00, C(6) 0·01, C(7) 0·00, C(8) 0·00, Br 0·03, N(9) 0·02]

Plane (II): C(12)—(14), N(15), C(16), N(17) $0{\cdot}8568X + 0{\cdot}0002Y + 0{\cdot}5156Z' = 9{\cdot}4876$

[C(12) 0·02, C(13) −0·01, C(14) 0·00, N(15) 0·01, C(16) 0·00, N(17) −0·02, N(11) 0·09, C(18) −0·03, C(24) 0·01]

Plane (III): S, C(21)—(23) $-0{\cdot}2745X - 0{\cdot}4211Y + 0{\cdot}8644Z' = 1{\cdot}3311$

[S 0·02, C(21) −0·02, C(22) −0·02, C(23) 0·02, N(19) −0·33, C(20) −0·17, C(26) −0·17]

Plane (IV): O(1), N(9), C(10), N(11) $0{\cdot}7944X - 0{\cdot}0599Y + 0{\cdot}6043Z' = 9{\cdot}5452$

[O(1) 0·00, N(9) 0·00, C(10) 0·00, N(11) 0·00]

* X, Y, and Z' are orthogonal co-ordinates in Å, along the crystallographic *a*, *b*, and *c** axes, respectively.

distorted. The dihedral angle between the planes defined by S, C(21), C(22) and C(21), C(22), C(23) is *ca.* 175°.

Although cyclobutane itself is known to be nonplanar, both planar and non-planar examples have been found for the four-membered ring of substituted cyclobutane compounds.[17-22] The dihedral angle between planes of the pyrimidine ring and the N–CHO group is *ca.* 81°.

The conformation of the molecule seems to be held by two intramolecular hydrogen bonds, one between O(2) and N(11), the other between N(9) and N(17). The distances of the hydrogen bonds are given in Table **3**. The mean distances of 0·96 Å for C–H and 0·84 Å for N–H are shorter than the internuclear separations obtained spectroscopically.[23] The packing is efficient with several contacts approaching the sum of the van der Waals radii; the shortest contacts, excluding hydrogen atoms, are 3·282 Å for O(2) · · · $C(26^{III})$.

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