respectivement avec l'oxygène O(2) du groupement HPO_4^{2-} et les deux protons de la molécule d'eau (*W*2).

La maille élémentaire renferme huit molécules d'eau; chaque molécule (*W*1) est liée à deux groupements HPO_4^{2-} par deux liaisons hydrogène du type O···H(*W*1). Contrairement à l'atome d'oxygène O(*W*1), la molécule d'eau (*W*2) pontée sur l'azote N(2) au moyen des deux liaisons hydrogène décrites précédemment, engage le doublet de son oxygène O(*W*2) dans une liaison hydrogène avec le proton acide du groupement monohydrogénomonophosphate HPO_4^{2-}. Ces liaisons hydrogènes assurent la cohésion et la stabilité de l'édifice cristallin.

Références

Averbuch-Pouchot, M. T. & Durif, A. (1987). *Acta Cryst.* **C43**, 1894–1896.

Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1987). *Acta Cryst.* **C43**, 1896–1898.

Bagieu-Beucher, M., Durif, A. & Guitel, J. C. (1989). *Acta Cryst.* **C45**, 421–423.

Enraf–Nonius (1980). *Structure Determination Package.* Enraf–Nonius, Delft, Pays-Bas.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Distributeur actuel Kluwer Academic Publishers, Dordrecht.)

Kamoun, S., Jouini, A. & Daoud, A. (1990). *C. R. Acad. Sci. Sér.* II, **310**, 733–738.

Kamoun, S., Jouini, A., Kamoun, M. & Daoud, A. (1989). *Acta Cryst.* **C45**, 481–482.

Acta Cryst. (1990). C**46**, 1483–1487

Structures of Thiamine Thiocyanate, Thiamine Thiocyanate Monohydrate and Thiamine Tetrafluoroborate Monohydrate

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Abstract. $C_{12}H_{17}N_4OS^+.SCN^-$ (1), $M_r = 323\cdot44$, monoclinic, $C2/c$, $a = 20\cdot764$ (2), $b = 13\cdot890$ (2), $c = 10\cdot704$ (2) Å, $\beta = 100\cdot00$ (1)°, $V = 3040\cdot5$ (7) Å^3, $Z = 8$, $D_x = 1\cdot413$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 3\cdot41$ cm^{-1}, $F(000) = 1360$, $T = 294$ K, $R = 0\cdot044$ for 1609 observed reflections; $C_{12}H_{17}N_4OS^+.SCN^-.H_2O$ (2), $M_r = 341\cdot46$, triclinic, $P\bar{1}$, $a = 13\cdot691$ (4), $b = 12\cdot075$ (3), $c = 11\cdot739$ (2) Å, $\alpha = 88\cdot34$ (2), $\beta = 115\cdot50$ (2), $\gamma = 106\cdot61$ (2)°, $V = 1668\cdot6$ (8) Å^3, $Z = 4$, $D_x = 1\cdot359$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 3\cdot18$ cm^{-1}, $F(000) = 720$, $T = 294$ K, $R = 0\cdot051$ for 4178 observed reflections; $C_{12}H_{17}N_4OS^+.BF_4^-.H_2O$ (3), $M_r = 370\cdot18$, monoclinic, $P2_1/n$, $a = 13\cdot060$ (2), $b = 11\cdot134$ (2), $c = 11\cdot896$ (2) Å, $\beta = 93\cdot30$ (1)°, $V = 1726\cdot9$ (4) Å^3, $Z = 4$, $D_x = 1\cdot424$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 2\cdot30$ cm^{-1}, $F(000) = 768$, $T = 294$ K, $R = 0\cdot069$ for 2341 observed reflections. In each crystal, the thiamine molecule captures an anion molecule in the vicinity of the C(2) catalytic site, through a hydrogen bond with C(2)H and an electrostatic interaction with the pyrimidine ring.

Introduction. Thiamine (vitamin B_1), as its pyrophosphate ester, is a cofactor for a number of metabolic enzymes catalyzing the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups (Krampitz, 1969). It is well established that the substrate (*e.g.* pyruvate anion) reacts with the coenzyme at the C(2) site of the thiazolium moiety to form a reaction intermediate, hydroxyethyl thiamine pyrophosphate (Breslow, 1958). As part of our X-ray investigations of thiamine–anion interactions as a model for thiamine–substrate interactions (Aoki & Yamazaki, 1985; Aoki, Yamazaki, Waragai & Itokawa, 1988; Archibong, Adeyemo, Aoki & Yamazaki, 1989), we report here the crystal struc-

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Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal size (mm)	0·17 × 0·20 × 0·28	0·15 × 0·34 × 0·39	0·31 × 0·37 × 0·50
Crystal shape	Columnar	Plate	Columnar
2θ range measured (°)	3·0–50·0	3·0–55·0	3·0–50·0
Scan mode	ω–2θ	ω for $2\theta \leq 30°$ ω–2θ for $2\theta > 30°$	ω for $2\theta \leq 30°$ ω–2θ for $2\theta > 30°$
Scan range (°)	1·5 + 0·5tanθ	1·5 + 0·5tanθ	1·7 + 0·5tanθ
No. of standard reflections	3	3	3
Variation in F_o of standard reflections (%)	±1·7	±2·7	±1·9
Data collected	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$
Unique data measured	2668	7814	3655
Unique data used [$F_o > 3\sigma(F_o)$]	1609	4178	2341
Scan speed (2θ) (° min^{-1})	4·0	4·0	4·0
Background counting (s)	5	5	5
Transmission factors*	0·98–1·01	0·98–1·03	0·97–1·02
Final number of variables	258	561	254
Weighting scheme w	$\sigma(F_o)^{-2}$	1·0 for $F_o \leq 100$ $10^4/F_o^2$ for $F_o > 100$	$\sigma(F_o)^{-2}$
R	0·044	0·051	0·069
wR	0·029	0·049	0·053
S	1·78	1·01	3·62
$(\Delta/\sigma)_{max}$	0·39	0·48	0·30
$(\Delta\rho)_{max}$ (e Å^{-3})	0·25	0·28	0·39

* Normalized to an average of unity.

Table 2. *Fractional atomic coordinates and equivalent isotropic temperature factors, with e.s.d.'s in parentheses, for thiamine*.SCN (1)

$$B = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
N(1′)	0·0323 (1)	0·2039 (2)	0·4249 (3)	2·8
C(2′)	0·0024 (2)	0·2725 (3)	0·4805 (3)	2·7
N(3′)	0·0102 (1)	0·3677 (2)	0·4678 (3)	2·5
C(4′)	0·0531 (1)	0·3986 (3)	0·3942 (3)	2·5
C(5′)	0·0864 (1)	0·3297 (3)	0·3288 (3)	2·3
C(6′)	0·0731 (2)	0·2348 (3)	0·3487 (3)	2·8
C(2′α)	−0·0448 (2)	0·2409 (3)	0·5637 (4)	4·1
N(4′α)	0·0628 (1)	0·4930 (2)	0·3878 (3)	3·5
C(3,5′)	0·1311 (1)	0·3563 (3)	0·2394 (3)	2·7
S(1)	0·29833 (5)	0·39285 (8)	0·47299 (9)	3·4
C(2)	0·2179 (2)	0·3728 (3)	0·4292 (3)	2·9
N(3)	0·1998 (1)	0·3729 (2)	0·3053 (2)	2·3
C(4)	0·2510 (2)	0·3880 (3)	0·2384 (3)	2·4
C(5)	0·3090 (2)	0·4004 (3)	0·3163 (3)	2·7
C(4α)	0·2377 (2)	0·3836 (3)	0·0960 (3)	3·7
C(5α)	0·3759 (2)	0·4154 (3)	0·2849 (3)	3·6
C(5β)	0·4137 (2)	0·4977 (3)	0·3599 (4)	3·9
O(5γ)	0·4217 (1)	0·4823 (2)	0·4931 (2)	4·0
S(11)	0·1479 (1)	0·3694 (1)	0·7089 (1)	4·6
C(11)	0·2280 (2)	0·3556 (3)	0·7538 (3)	3·7
N(11)	0·2828 (1)	0·3462 (2)	0·7800 (3)	5·0

tures of thiamine thiocyanate (1), thiamine thiocyanate monohydrate (2) and thiamine tetrafluoroborate monohydrate (3).

Experimental. Compounds (1), (2) and (3) were prepared from thiaminium.$(SCN)_2$ and $Fe(OAc)_2$, thiaminium.$(SCN)_2$ and $Cu(OAc)_2$, and thiaminium.$(BF_4)_2$ and $Cd(OAc)_2$, respectively (each in 2:1 molar ratio in warm methanol).

Cell parameters were determined on a Rigaku AFC four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71073 Å) from 20 reflections [$21 < 2\theta < 28°$ for (1), $23 < 2\theta < 35°$ for (2), and $22 < 2\theta < 33°$ for (3)]. Details of the data collection and structure refinement are summarized in Table 1. Intensities were corrected for Lp effects but not for absorption.

Table 3. *Fractional atomic coordinates and equivalent isotropic temperature factors, with e.s.d.'s in parentheses, for thiamine*.SCN.H_2O (2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
N(1′*A*)	0·2830 (2)	0·0018 (3)	0·1706 (3)	3·9
C(2′*A*)	0·3002 (3)	0·0963 (3)	0·2415 (4)	3·5
N(3′*A*)	0·3965 (2)	0·1528 (3)	0·3411 (3)	3·3
C(4′*A*)	0·4866 (3)	0·1127 (3)	0·3738 (3)	3·1
C(5′*A*)	0·4759 (3)	0·0107 (3)	0·3063 (3)	3·2
C(6′*A*)	0·3727 (3)	−0·0386 (3)	0·2072 (4)	3·9
C(2′α*A*)	0·2027 (3)	0·1455 (4)	0·2057 (4)	5·0
N(4′α*A*)	0·5826 (2)	0·1739 (3)	0·4712 (3)	4·1
C(3,5′*A*)	0·5691 (3)	−0·0443 (3)	0·3445 (4)	3·7
S(1*A*)	0·7416 (1)	0·1146 (1)	0·1590 (1)	5·0
C(2*A*)	0·6385 (3)	0·0816 (4)	0·2069 (4)	4·1
N(3*A*)	0·6504 (2)	0·0043 (3)	0·2886 (3)	3·2
C(4*A*)	0·7450 (3)	−0·0335 (3)	0·3165 (3)	3·1
C(5*A*)	0·8037 (3)	0·0183 (3)	0·2535 (3)	3·6
C(4α*A*)	0·7692 (4)	−0·1212 (4)	0·4084 (4)	4·6
C(5α*A*)	0·9098 (3)	0·0011 (4)	0·2581 (4)	4·5
C(5β*A*)	0·8988 (3)	−0·0289 (4)	0·1286 (4)	4·3
O(5γ*A*)	0·8958 (2)	0·0709 (2)	0·0621 (2)	4·5
N(1′*B*)	0·6805 (2)	0·5165 (3)	0·7927 (3)	3·8
C(2′*B*)	0·6656 (3)	0·4280 (3)	0·7151 (3)	3·5
N(3′*B*)	0·5693 (2)	0·3705 (3)	0·6174 (3)	3·2
C(4′*B*)	0·4754 (3)	0·4023 (3)	0·5934 (3)	3·0
C(5′*B*)	0·4833 (3)	0·4953 (3)	0·6708 (3)	3·0
C(6′*B*)	0·5879 (3)	0·5489 (3)	0·7673 (3)	3·5
C(2′α*B*)	0·7679 (3)	0·3897 (4)	0·7415 (4)	5·0
N(4′α*B*)	0·3804 (2)	0·3434 (3)	0·4946 (3)	3·6
C(3,5′*B*)	0·3858 (3)	0·5412 (3)	0·6462 (3)	3·3
S(1*B*)	0·2537 (1)	0·3636 (1)	0·8601 (1)	4·2
C(2*B*)	0·3446 (3)	0·4081 (3)	0·7958 (4)	3·5
N(3*B*)	0·3169 (2)	0·4826 (2)	0·7128 (2)	2·8
C(4*B*)	0·2187 (3)	0·5077 (3)	0·6970 (3)	2·9
C(5*B*)	0·1734 (3)	0·4500 (3)	0·7711 (3)	3·2
C(4α*B*)	0·1768 (3)	0·5913 (4)	0·6060 (4)	4·6
C(5α*B*)	0·0703 (3)	0·4543 (4)	0·7844 (4)	4·1
C5β*B*)	0·0973 (3)	0·4841 (4)	0·9214 (4)	4·3
O(5γ*B*)	0·1258 (2)	0·3911 (3)	0·9931 (2)	4·5
S(11*A*)	0·8471 (1)	0·1418 (1)	0·6242 (1)	5·1
C(11*A*)	0·9316 (3)	0·1938 (4)	0·5571 (4)	4·1
N(11*A*)	0·9935 (3)	0·2304 (4)	0·5128 (4)	5·6
S(11*B*)*	0·5728 (2)	0·2847 (2)	0·9410 (2)	7·0
C(11*B*)*	0·4986 (7)	0·2544 (7)	1·0230 (6)	5·9
N(11*B*)*	0·4320 (6)	0·2166 (6)	1·0571 (8)	8·4
S(11*B*′)*	0·4669 (5)	0·2518 (5)	1·0657 (5)	8·2
C(11*B*′)*	0·518 (1)	0·251 (1)	0·967 (1)	5·1
N(11*B*′)*	0·539 (1)	0·243 (1)	0·896 (1)	8·1
O(*WA*)	1·0159 (3)	0·3022 (2)	0·1482 (3)	4·9
O(*WB*)	1·1491 (2)	0·3541 (3)	0·4119 (3)	5·2

* Disordered SCN group; occupancy factors: 0·68 for S(11*B*), C(11*B*) and N(11*B*) and 0·32 for S(11*B*′), C(11*B*′) and N(11*B*′).

Table 4. *Fractional atomic coordinates and equivalent isotropic temperature factors, with e.s.d.'s in parentheses, for thiamine*.$BF_4.H_2O$ (3)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
N(1′)	0·9450 (2)	−0·1612 (3)	0·5814 (2)	3·0
C(2′)	0·9045 (3)	−0·2353 (3)	0·5023 (3)	3·0
N(3′)	0·8362 (2)	−0·2052 (3)	0·4191 (2)	2·9
C(4′)	0·8017 (3)	−0·0906 (3)	0·4150 (3)	2·5
C(5′)	0·8392 (2)	−0·0062 (3)	0·4969 (3)	2·2
C(6′)	0·9106 (3)	−0·0464 (3)	0·5745 (3)	2·8
C(2′α)	0·9376 (3)	−0·3632 (4)	0·5077 (4)	4·9
N(4′α)	0·7317 (2)	−0·0634 (3)	0·3325 (2)	3·4
C(3,5′)	0·8085 (3)	0·1233 (3)	0·4949 (3)	2·6
S(1)	0·5479 (1)	0·1134 (1)	0·6462 (1)	3·7
C(2)	0·6546 (3)	0·0594 (3)	0·5929 (3)	3·0
N(3)	0·7084 (2)	0·1445 (2)	0·5460 (2)	2·2
C(4)	0·6649 (3)	0·2583 (3)	0·5521 (3)	2·3
C(5)	0·5758 (3)	0·2573 (3)	0·6037 (3)	2·5
C(4α)	0·7179 (3)	0·3653 (3)	0·5065 (4)	4·1
C(5α)	0·5103 (3)	0·3650 (4)	0·6251 (3)	3·5
C(5β)	0·4045 (3)	0·3386 (4)	0·6619 (3)	3·8
O(5γ)	0·4044 (2)	0·2619 (2)	0·7587 (2)	3·3
O(*W*)	0·6402 (2)	0·1657 (3)	0·2872 (2)	5·2
B	0·6240 (4)	−0·2677 (5)	0·6866 (4)	5·3
F(1)*	0·5601 (4)	−0·1990 (5)	0·6220 (4)	7·5
F(2)*	0·7165 (4)	−0·2101 (5)	0·6944 (6)	10·1
F(3)*	0·6490 (7)	−0·3701 (6)	0·6421 (7)	15·0
F(4)*	0·5837 (5)	−0·2734 (7)	0·7840 (5)	13·9
F(1′)*	0·6185 (8)	−0·1934 (7)	0·7712 (6)	12·7
F(2′)*	0·6809 (7)	−0·3622 (10)	0·7220 (7)	14·5
F(3′)*	0·5344 (6)	−0·3365 (7)	0·6747 (8)	11·9
F(4′)*	0·6369 (9)	−0·2185 (7)	0·5948 (6)	14·4

* Disordered F atoms; occupancy factors: 0·55 for F(1)–F(4) and 0·45 for F(1′)–F(4′).

The structures were solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares, minimizing the function $\sum w(F_o - |F_c|)^2$. One of the two SCN^- anions in (2) and a BF_4^- anion in (3) were disordered, each in two positions; the occupancy factors were estimated on the basis of their electron densities. All non-H atoms including disordered anions were refined anisotropically. All H atoms were located from difference Fourier maps, and their atomic coordinates and isotropic temperature factors, which were refined for (1) and (2) but fixed for (3) ($B = 5{\cdot}0$ Å^2), were included in the structure-factor calculations in the final cycles of the refinements. Final atomic parameters with their e.s.d.'s are listed in Tables 2–4.* Atomic scattering factors and anomalous-dispersion corrections for F and S were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the *UNICS*III program system (Sakurai & Kobayashi, 1979) on a FACOM780 computer.

Table 5. *Bond lengths* (Å) *and angles* (°) *and relevant torsion angles* (°) *of thiamine molecules in thiamine*.SCN (1), *thiamine*.SCN.H_2O (2) *and thiamine*.$BF_4.H_2O$ (3) *with e.s.d.'s in parentheses*

	(1)	(2)		(3)
		A	*B*	
N(1′)—C(2′)	1·332 (5)	1·335 (6)	1·336 (6)	1·338 (5)
C(2′)—N(3′)	1·343 (5)	1·332 (4)	1·325 (4)	1·337 (5)
N(3′)—C(4′)	1·357 (4)	1·352 (5)	1·358 (5)	1·354 (5)
C(4′)—C(5′)	1·432 (5)	1·420 (6)	1·415 (6)	1·420 (5)
C(5′)—C(6′)	1·372 (5)	1·360 (4)	1·367 (4)	1·350 (5)
C(6′)—N(1′)	1·344 (5)	1·343 (6)	1·343 (6)	1·355 (5)
C(2′)—C(2′α)	1·499 (6)	1·506 (7)	1·503 (7)	1·488 (6)
C(4′)—N(4′α)	1·330 (5)	1·335 (4)	1·328 (4)	1·337 (4)
C(5′)—C(3,5′)	1·491 (5)	1·499 (6)	1·502 (6)	1·496 (5)
C(3,5′)—N(3)	1·495 (4)	1·499 (6)	1·493 (6)	1·492 (4)
S(1)—C(2)	1·678 (3)	1·678 (5)	1·677 (5)	1·676 (4)
C(2)—N(3)	1·314 (4)	1·311 (5)	1·315 (5)	1·322 (5)
N(3)—C(4)	1·396 (4)	1·397 (6)	1·394 (5)	1·393 (5)
C(4)—C(5)	1·353 (4)	1·336 (6)	1·345 (6)	1·347 (5)
C(5)—S(1)	1·733 (4)	1·728 (4)	1·730 (4)	1·726 (4)
C(4)—C(4α)	1·502 (5)	1·491 (6)	1·493 (6)	1·495 (5)
C(5)—C(5α)	1·498 (5)	1·502 (7)	1·501 (7)	1·503 (5)
C(5α)—C(5β)	1·533 (5)	1·506 (7)	1·516 (6)	1·503 (6)
C(5β)—O(5γ)	1·423 (5)	1·417 (5)	1·426 (6)	1·434 (5)
N(1′)—C(2′)—N(3′)	125·8 (3)	126·2 (4)	126·3 (4)	125·9 (3)
C(2′)—N(3′)—C(4′)	118·3 (3)	117·7 (4)	117·8 (4)	118·0 (3)
N(3′)—C(4′)—C(5′)	119·6 (3)	120·3 (3)	119·8 (3)	119·9 (3)
C(4′)—C(5′)—C(6′)	116·0 (3)	115·8 (4)	116·9 (4)	116·6 (3)
C(5′)—C(6′)—N(1′)	124·4 (3)	125·0 (4)	123·6 (4)	124·6 (3)
C(6′)—N(1′)—C(2′)	115·8 (3)	115·0 (3)	115·7 (3)	115·0 (3)
N(1′)—C(2′)—C(2′α)	117·4 (3)	117·6 (3)	116·8 (3)	117·3 (3)
N(3′)—C(2′)—C(2′α)	116·9 (3)	116·2 (4)	116·9 (4)	116·9 (3)
N(3′)—C(4′)—N(4′α)	117·5 (3)	116·0 (4)	116·4 (4)	116·9 (3)
C(5′)—C(4′)—N(4′α)	122·9 (3)	123·8 (4)	123·9 (4)	123·3 (3)
C(4′)—C(5′)—C(3,5′)	123·8 (3)	123·0 (3)	123·3 (3)	123·0 (3)
C(6′)—C(5′)—C(3,5′)	120·2 (3)	121·2 (4)	119·7 (4)	120·3 (3)
C(5′)—C(3,5′)—N(3)	112·7 (3)	113·6 (3)	112·9 (3)	112·7 (3)
C(3,5′)—N(3)—C(2)	123·9 (3)	124·2 (4)	124·1 (4)	123·9 (3)
C(3,5′)—N(3)—C(4)	122·0 (3)	122·0 (3)	122·1 (3)	122·4 (3)
S(1)—C(2)—N(3)	112·2 (3)	112·4 (4)	112·5 (3)	112·1 (3)
C(2)—N(3)—C(4)	114·1 (3)	113·8 (4)	113·7 (4)	113·7 (3)
N(3)—C(4)—C(5)	112·3 (3)	112·1 (3)	112·3 (3)	112·5 (3)
C(4)—C(5)—S(1)	109·8 (3)	110·7 (4)	110·3 (3)	110·1 (3)
C(5)—S(1)—C(2)	91·6 (2)	91·0 (2)	91·2 (2)	91·6 (2)
N(3)—C(4)—C(4α)	119·5 (3)	119·6 (4)	119·8 (4)	120·5 (3)
C(5)—C(4)—C(4α)	128·2 (3)	128·3 (4)	127·9 (4)	127·0 (3)
S(1)—C(5)—C(5α)	120·3 (2)	121·3 (2)	120·6 (3)	124·0 (3)
C(4)—C(5)—C(5α)	129·8 (3)	128·0 (4)	129·1 (4)	125·8 (3)
C(5)—C(5α)—C(5β)	113·4 (3)	112·9 (3)	111·8 (3)	115·7 (3)
C(5α)—C(5β)—O(5γ)	111·9 (3)	108·6 (4)	109·6 (4)	113·2 (3)
φ_T	−5·8 (4)	−4·6 (5)	7·3 (5)	3·0 (5)
φ_P	86·6 (4)	−87·7 (5)	91·0 (4)	82·4 (4)
$\varphi_{5\alpha}$	−48·8 (4)	−53·8 (5)	53·7 (5)	−14·2 (5)
$\varphi_{5\beta}$	58·8 (4)	70·4 (5)	−67·4 (4)	54·3 (4)

Note. Torsion angle conformational terms defined by Pletcher, Sax, Blank & Wood (1977): φ_T = C(5′)—C(3,5′)—N(3)—C(2), φ_P = N(3)—C(3,5′)—C(5′)—C(4′), $\varphi_{5\alpha}$ = S(1)—C(5)—C(5α)—C(5β), $\varphi_{5\beta}$ = C(5)—C(5α)—C(5β)—O(5γ).

Discussion. Bond distances and angles and relevant torsion angles of thiamine molecules are listed in Table 5. Molecular structures are shown in Fig. 1 and crystal packings in Fig. 2. The asymmetric unit of (2) consists of two independent chemical units.

The thiamine moiety adopts the usually observed *F* conformation (Pletcher, Sax, Blank & Wood, 1977) (Table 5); the dihedral angle between the pyrimidine and thiazolium rings is 96·5 (1)° for (1), 90·6 (1) (*A* molecule) and 86·1 (1)° (*B* molecule) for (2), and 97·3 (1)° for (3). The C(5) hydroxyethyl side chain folds back towards the thiazolium moiety to make a close contact between O(5γ) and S(1): 2·822 (3) Å for (1), 2·961 (4) (*A* molecule) and 2·887 (4) Å (*B* molecule) for (2), and 2·885 (3) Å for (3) [sum of van der

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions, bond lengths and angles of thiocyanate and tetrafluoroborate anions, and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52812 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Waals radii for O···S = 3·32 (3) Å (Bondi, 1964)]. A thiocyanate anion, N(11)—C(11)—S(11) in (1) or N(11*B*)—C(11*B*)—S(11*B*) in (2), attaches to the thiazolium ring *via* a hydrogen bond with the acidic C(2)H.* This anion molecule further makes a close contact with the pyrimidine ring of the same thiamine molecule.* There is another type of thiamine–NCS^- interaction: an NCS^- ion, N(11)—C(11)—S(11) in (1) or N(11*A*)—C(11*A*)—S(11*A*) in (2), bridges between the pyrimidine and the thiazolium rings [*A* molecule for (2)] through an N(4′*α*)—H···S(11) hydrogen bond and an SCN^-···thiazolium-ring electrostatic interaction.* Despite a geometrical difference between linear NCS^- and tetrahedral BF_4^- anions, a BF_4^- anion in (3) is also located at the same position as that of

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* See deposition footnote.

* See deposition footnote.

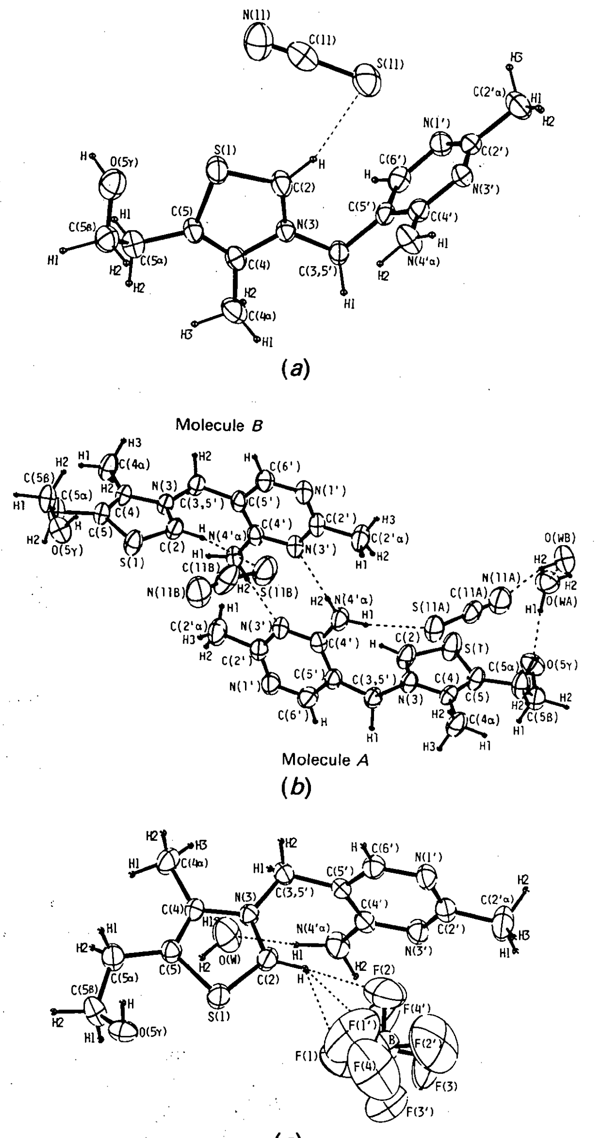

Fig. 1. Molecular structures of (*a*) thiamine.SCN (1), (*b*) thiamine.-SCN.H_2O (2) and (*c*) thiamine.BF_4.H_2O (3). The broken lines denote hydrogen bonds. A disordered thiocyanate ion S(11*B*′)—C(11*B*′)—N(11*B*′) is omitted for clarity in (*b*).

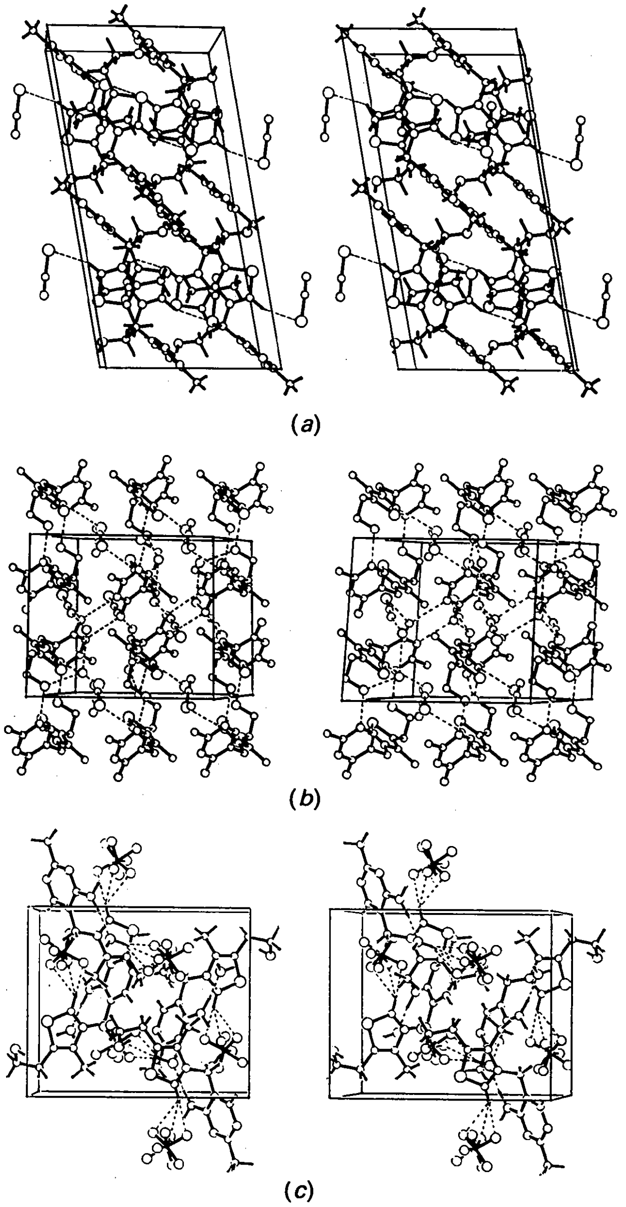

Fig. 2. Crystal-packing arrangements of (*a*) thiamine.SCN (1) viewed down the *b* axis with the *c* axis horizontal and the *a* axis vertical, (*b*) thiamine.SCN.H_2O (2) viewed down the *a* axis with the *b* axis horizontal and the *c* axis vertical, and (*c*) thiamine.BF_4.H_2O (3) viewed down the *c* axis with the *a* axis horizontal and the *b* axis vertical. Broken lines denote hydrogen bonds.

an NCS$^-$ anion in (1) or (2), that is, the BF_4^- anion forms a hydrogen bond with thiazolium C(2)H and it further contacts electrostatically with the pyrimidine ring.* Analogously to the above-mentioned NCS$^-$ anion bridge in (1) and (2), there is a water bridge between the pyrimidine and the thiazolium rings in (2) and (3), that is, a water molecule, O(*WB*) in (2) or O(*W*) in (3), forms a hydrogen bond with N(4′*α*)H and also takes part in an electrostatic interaction with the thiazolium ring [*B* molecule for (2); not shown in Fig. 1(*b*)].* This type of water bridge has often been observed in other hydrated thiamine structures with the *F* conformation, *e.g.* thiamine.Cl.H_2O (Pletcher, Sax, Sengupta, Chu & Yoo, 1972), thiamine.picrolonate.$2H_2O$ (Shin, Pletcher, Blank & Sax, 1977), thiaminepyrophosphate.$4{\cdot}5H_2O$ (Pletcher, Blank, Wood & Sax, 1979), thiamine.PF_6.H_2O (Aoki, Yamazaki, Waragai & Itokawa, 1988), thiaminium.$(PF_6)_2$.$4H_2O$ (Aoki *et al.*, 1988) and thiamine monophosphate.PF_6.$2H_2O$ (Aoki *et al.*, 1988). This suggests that the water bridge stabilizes the *F* conformation of thiamine.

A base–base pairing through a pair of N(4′*α*)—H···N(3′) hydrogen bonds forms across a centre of symmetry in (1) (not shown in Fig. 1*a*) and between molecules *A* and *B* in (2), while it does not in (3). An O(5*γ*)—H···N(1′) hydrogen bond, which is commonly formed in (1)–(3), creates a thiamine–thiamine self-dimer in (1) and (2), each across a centre of symmetry [*i.e.* between *A* and *A* and between *B* and *B* molecules in (2)] while it creates a polymeric molecular array of thiamines in (3).

In summary, this work presents additional examples showing the thiamine–anion complexation, where an anion molecule forms a hydrogen bond with the acidic C(2)H and it further interacts electrostatically with the pyrimidine ring of the same thiamine molecule with the *F* conformation, thus serving as a model for the substrate anion fixation near the catalytic C(2) site in the enzyme system.

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* See deposition footnote.

References

Aoki, K. & Yamazaki, H. (1985). *J. Am. Chem. Soc.* **107**, 6242–6249.

Aoki, K., Yamazaki, H., Waragai, K. & Itokawa, H. (1988). *Acta Cryst.* C**44**, 1949–1955.

Archibong, E., Adeyemo, A., Aoki, K. & Yamazaki, H. (1989). *Inorg. Chim. Acta*, **156**, 77–83.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Breslow, R. (1958). *J. Am. Chem. Soc.* **80**, 3719–3726.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Krampitz, L. O. (1969). *Annu. Rev. Biochem.* **38**, 213–240.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Pletcher, J., Blank, G., Wood, M. & Sax, M. (1979). *Acta Cryst.* B**35**, 1633–1637.

Pletcher, J., Sax, M., Blank, G. & Wood, M. (1977). *J. Am. Chem. Soc.* **99**, 1396–1403.

Pletcher, J., Sax, M., Sengupta, S., Chu, J. & Yoo, C. S. (1972). *Acta Cryst.* B**28**, 2928–2935.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Shin, W., Pletcher, J., Blank, G. & Sax, M. (1977). *J. Am. Chem. Soc.* **99**, 3491–3499.

Acta Cryst. (1990). C**46**, 1487–1490

Structure of 3,5-Bis(dimethylamino)-6-phenyl-1,2,4-triazine 1-Imide

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Abstract. $C_{13}H_{18}N_6$, $M_r = 258{\cdot}32$, orthorhombic, $P2_12_12$, $a = 15{\cdot}095$ (3), $b = 16{\cdot}333$ (3), $c = 5{\cdot}643$ (1) Å, $V = 1391{\cdot}3$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}233$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}56$ mm^{-1}, $F(000) = 552$, $T = 293$ (1) K, final $R = 0{\cdot}042$, $wR = 0{\cdot}046$ for 2500 independent reflections. The 1,2,4 triazide ring is not strictly planar, the phenyl ring makes an angle of −63·5 (1)° with the plane through N1, N2, C5, N11. The bond distances in the triazinium imide, particularly the N1—N11 (imide) at 1·296 (2) Å, indicate that canonical forms involving an exocyclic N—N double bond at N1

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