Rodier, Céolin & Astoin, 1985; Werninck, Blair, Milburn, Ando, Bloor, Motevalli & Hursthouse, 1985), and seems to have single-bond character. It may be considered that the bond has been lengthened because of two bulky groups arranged *cis* to each other or a conjugation could not extend to C(4)—C(7) due to the heterocyclic four-membered ring containing C(4). No shorter contact than van der Waals radii was found between molecules in the crystal structure.

We thank Dr T. Takaya, Central Research Laboratories, Fujisawa Pharmaceutical Co. Ltd, for helpful discussion.

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Structure of Thiamin Naphthalene-1,5-disulfonate Monohydrate

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(*Received* 14 *April* 1986; *accepted* 29 *July* 1986)

Abstract. 3-[(4-Amino-2-methyl-5-pyrimidinio)-methyl]-5-(2-hydroxyethyl)-4-methylthiazolium naphthalene-1,5-disulfonate monohydrate, $C_{12}H_{18}N_4OS^{2+}.C_{10}H_6(SO_3^-)_2.H_2O$, $M_r = 570{\cdot}65$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}887\ (2)$, $b = 15{\cdot}754\ (3)$, $c = 20{\cdot}101\ (4)$ Å, $V = 2498\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}517$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 30{\cdot}54$ cm^{-1}, $F(000) = 1192$, $T = 295$ K, $R = 0{\cdot}040$ for 1798 observed reflections. Thiamin maintains a characteristic *F* conformation, even though it forms a molecular complex with a large molecular anion. The structure shows a partial ring-stacking interaction between the thiazolium ring of thiamin and the naphthalene ring, which has not been observed previously. S(1) is the principal site for interaction. The crystal packing is dominated by an extensive hydrogen-bonding network.

Introduction. Thiamin (vitamin B_1), in the form of pyrophosphate ester, is a coenzyme for enzyme systems catalyzing the transfer of aldehyde or acyl groups such as pyruvate decarboxylase and transketolase (Krampitz, 1969; Gallo, Mieyal & Sable, 1978). Although the nature of the enzyme catalytic site is not completely known, it is generally believed that the ring-stacking interaction between thiamin and tryptophan may play an important role in coenzyme binding. Accordingly, numerous attempts have been made to obtain crystalline complexes between thiamin and tryptophan or indole compounds, the crystal structures of which may show the detailed interaction mode at the atomic level, but these have so far failed. However, we obtained crystals of the molecular complex (thiamin 1,5-salt) between thiamin and naphthalene-1,5-disulfonate (NDS) anion. Its structure may provide an insight into the interaction mode of thiamin with a large π-electron system.

Experimental. Thiamin 1,5-salt prepared by mixing 10% aqueous solution of thiamin chloride hydrochloride and naphthalene-1,5-disulfonic acid disodium salt. Colorless tabular crystals obtained from an aqueous solution of 1,5-salt by slow evaporation at room temperature; crystal *ca* 0·2 × 0·3 × 0·5 mm, Rigaku AFC diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $2\theta < 120°$, ω–2θ scan, scan speed 4° min^{-1} in 2θ, ω-scan width $(1{\cdot}3 + 0{\cdot}5\tan\theta)°$, background measured for 12 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values

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for 24 centered reflections with $22 < 2\theta < 50°$; intensity checks for three standard reflections showed little ($\pm 0{\cdot}6\%$) variation; 2147 independent reflections (h 0 to 8, k 0 to 17, l 0 to 22), 1798 (83·7%) observed with $I > 3\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined with *SHELX*76 (Sheldrick, 1976) by full-matrix least squares on F with anisotropic thermal parameters, H atoms identified on a difference map and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = k/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F)$ from counting statistics, k and g optimized in the least-squares procedure ($k = 1{\cdot}00$, $g = 0{\cdot}0088$); $wR = 0{\cdot}044$ for 1798 observed reflections, 398 variables, $R = 0{\cdot}058$ for all data, $S = 0{\cdot}63$, $(\Delta/\sigma)_{max} = 0{\cdot}255$ [thermal parameter of C(2′α)] in final refinement cycle. Max. and min. heights in final difference map 0·34 and $-0{\cdot}35$ e Å^{-3}, respectively. Handedness of the crystal correctly established since $R_{obs} = 0{\cdot}050$ and $wR = wR_{obs} = 0{\cdot}057$ for the opposite handedness. All calculations performed with *SHELX*76 on a VAX 11/780. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1.* Bond distances along with the atomic numbering scheme are shown in Fig. 1. Bond angles are listed in Table 2. The hydroxyethyl side chain in the thiamin cation is dynamically disordered even though the terminal O(5γ) is involved in the electrostatic interaction with the S(1) atom and hydrogen-bonded to the water molecule. Accordingly, the bonds involving the C(5), C(5α) and C(5β) atoms appear abnormally short. Similar disordering phenomena have been observed in the Cu(thiamin)Cl_2 structure (Cramer, Maynard & Evangelista, 1984). Otherwise, all of the molecular dimensions of the thiamin cation are in good agreement with those of thiamin containing a protonated pyrimidine ring (Cramer, Maynard & Ibers, 1981).

The pyrimidine and the thiazolium rings are planar with maximum deviations of 0·022 (4) and 0·007 (5) Å, respectively. The two ring planes make a dihedral angle of 88·9°. The thiamin cation exhibits the characteristic F conformation† with torsion angles of $\varphi_T = C(5')-$

Table 1. *Final positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	993 (2)	5629 (1)	7278 (1)	0·054
C(2)	284 (6)	5623 (3)	6488 (2)	0·038
N(3)	1357 (5)	5990 (2)	6082 (2)	0·032
C(4)	2817 (6)	6315 (3)	6389 (2)	0·036
C(4α)	4127 (7)	6747 (4)	5984 (3)	0·051
C(5)	2811 (7)	6158 (4)	7037 (2)	0·047
C(5α)	4209 (9)	6361 (6)	7534 (3)	0·084
C(5β)	3831 (11)	6572 (9)	8155 (4)	0·139
O(5γ)	2399 (8)	6605 (5)	8426 (3)	0·121
C(35′)	1022 (7)	6120 (3)	5358 (2)	0·035
N(1′)	−3014 (5)	5342 (3)	4626 (2)	0·034
C(2′)	−2605 (6)	4538 (3)	4453 (2)	0·033
C(2′α)	−3909 (8)	4042 (4)	4094 (3)	0·057
N(3′)	−1126 (5)	4203 (2)	4585 (2)	0·034
C(4′)	36 (6)	4679 (3)	4913 (2)	0·032
N(4′α)	1482 (7)	4323 (3)	5045 (3)	0·048
C(5′)	−299 (6)	5544 (3)	5084 (2)	0·028
C(6′)	−1862 (6)	5843 (3)	4933 (2)	0·033
S(1*N*)	944 (1)	3217 (1)	8913 (1)	0·033
O(1*N*)	−818 (4)	2946 (2)	8939 (2)	0·045
O(2*N*)	1158 (4)	4072 (2)	9194 (2)	0·041
O(3*N*)	2108 (5)	2605 (2)	9203 (2)	0·049
S(2*N*)	5575 (1)	4133 (1)	6089 (1)	0·035
O(4*N*)	5425 (5)	3305 (2)	5771 (2)	0·055
O(5*N*)	4348 (5)	4733 (2)	5834 (2)	0·045
O(6*N*)	7291 (4)	4447 (3)	6079 (2)	0·056
C(1*N*)	1483 (6)	3308 (3)	8051 (2)	0·030
C(2*N*)	285 (6)	3101 (3)	7589 (3)	0·041
C(3*N*)	619 (7)	3170 (4)	6910 (2)	0·046
C(4*N*)	2157 (6)	3439 (3)	6697 (2)	0·038
C(5*N*)	5076 (6)	3968 (3)	6946 (2)	0·031
C(6*N*)	6309 (6)	4144 (3)	7403 (2)	0·038
C(7*N*)	5992 (7)	4043 (4)	8082 (2)	0·044
C(8*N*)	4432 (7)	3776 (3)	8302 (2)	0·037
C(9*N*)	3123 (5)	3590 (3)	7845 (2)	0·027
C(10*N*)	3439 (6)	3669 (3)	7148 (2)	0·027
O(*W*)	2967 (7)	2685 (3)	4736 (3)	0·079

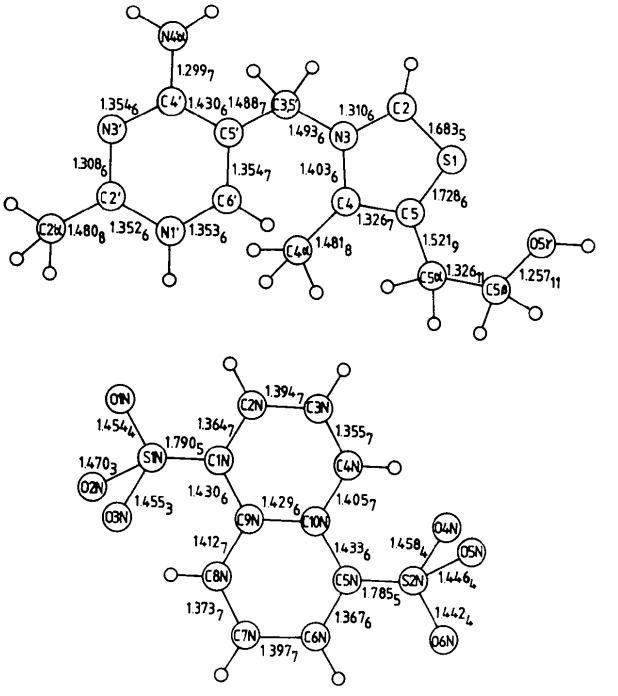

Fig. 1. Numbering scheme and bond distances (Å) with e.s.d.'s as subscripts.

* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, bond distances and angles involving the H atoms, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43296 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The conformation of thiamin with respect to the methylene bridge carbon joining the thiazolium and pyrimidine rings can be defined in terms of the torsion angles φ_T and φ_P. F is used to designate the conformation which is characteristic of thiamin when it is free of substituents on C(2). For more details, see footnote 13 in Pletcher, Sax, Blank & Wood (1977).

Table 2. *Bond angles* (°) *with e.s.d.'s in parentheses*

N(3)–C(2)–S(1)	111·7 (4)	C(4)–N(3)–C(2)	114·7 (4)
C(4)–C(5)–S(1)	111·6 (4)	C(4α)–C(4)–N(3)	119·9 (4)
C(5)–S(1)–C(2)	90·9 (2)	C(5)–C(4)–N(3)	111·1 (4)
C(5)–C(4)–C(4α)	128·9 (5)	C(5α)–C(5)–S(1)	121·3 (4)
C(5α)–C(5)–C(4)	127·1 (5)	C(5β)–C(5α)–C(5)	120·5 (6)
O(5γ)–C(5β)–C(5α)	128·5 (8)	C(35′)–N(3)–C(2)	123·6 (4)
C(35′)–N(3)–C(4)	121·6 (4)	C(2′α)–C(2′)–N(1′)	117·0 (4)
N(3′)–C(2′)–N(1′)	122·5 (4)	N(3′)–C(2′)–C(2′α)	120·4 (4)
C(4′)–N(3′)–C(2′)	118·7 (4)	C(4′)–C(5′)–C(35′)	122·8 (4)
N(4′α)–C(4′)–N(3′)	117·0 (4)	C(5′)–C(35′)–N(3)	113·7 (4)
C(5′)–C(4′)–N(3′)	121·3 (4)	C(5′)–C(4′)–N(4′α)	121·6 (4)
C(5′)–C(6′)–N(1′)	120·7 (5)	C(6′)–N(1′)–C(2′)	120·2 (4)
C(6′)–C(5′)–C(35′)	120·6 (4)	C(6′)–C(5′)–C(4′)	116·5 (4)
O(2*N*)–S(1*N*)–O(1*N*)	112·4 (2)	O(3*N*)–S(1*N*)–O(1*N*)	113·3 (2)
O(3*N*)–S(1*N*)–O(2*N*)	112·4 (2)	O(4*N*)–S(2*N*)–O(5*N*)	112·0 (2)
O(6*N*)–S(2*N*)–O(5*N*)	113·5 (2)	O(6*N*)–S(2*N*)–O(4*N*)	112·1 (2)
C(1*N*)–S(1*N*)–O(1*N*)	106·6 (2)	C(1*N*)–S(1*N*)–O(2*N*)	105·7 (2)
C(1*N*)–S(1*N*)–O(3*N*)	107·0 (2)	C(2*N*)–C(1*N*)–S(1*N*)	118·4 (4)
C(3*N*)–C(2*N*)–C(1*N*)	121·1 (5)	C(4*N*)–C(3*N*)–C(2*N*)	120·2 (5)
C(5*N*)–S(2*N*)–O(5*N*)	106·8 (2)	C(5*N*)–S(2*N*)–O(4*N*)	106·0 (2)
C(5*N*)–S(2*N*)–O(6*N*)	105·7 (2)	C(5*N*)–C(10*N*)–C(4*N*)	123·4 (4)
C(6*N*)–C(5*N*)–S(2*N*)	117·5 (3)	C(7*N*)–C(6*N*)–C(5*N*)	120·4 (4)
C(8*N*)–C(7*N*)–C(6*N*)	120·6 (5)	C(8*N*)–C(9*N*)–C(1*N*)	122·6 (4)
C(9*N*)–C(1*N*)–S(1*N*)	121·3 (3)	C(9*N*)–C(1*N*)–C(2*N*)	120·3 (4)
C(9*N*)–C(8*N*)–C(7*N*)	120·6 (4)	C(9*N*)–C(10*N*)–C(4*N*)	119·0 (4)
C(9*N*)–C(10*N*)–C(5*N*)	117·6 (4)	C(10*N*)–C(4*N*)–C(3*N*)	121·4 (4)
C(10*N*)–C(5*N*)–S(2*N*)	121·3 (3)	C(10*N*)–C(5*N*)–C(6*N*)	121·1 (4)
C(10*N*)–C(9*N*)–C(1*N*)	118·0 (4)	C(10*N*)–C(9*N*)–C(8*N*)	119·5 (4)

C(35′)–N(3)–C(2) = −20·9 (5) and φ_P = N(3)–C(35′)–C(5′)–C(4′) = −79·0 (6)°. The torsion angles $\varphi_{5\alpha}$ = S(1)–C(5)–C(5α)–C(5β) = −36·5 (8) and $\varphi_{5\beta}$ = C(5)–C(5α)–C(5β)–O(5γ) = 3·0 (9)° are quite different from the values frequently found of 60 to 90°. This deviation is presumably due to the poorly located C(5β) position.

The structure of the NDS anion has not previously been determined. The C–C bonds can be sorted into three different groups based on the magnitudes of the bond distances. The C(1*N*)–C(2*N*), C(3*N*)–C(4*N*), C(5*N*)–C(6*N*) and C(7*N*)–C(8*N*) bonds are shortest [av. 1·365 (8) Å] and the C(1*N*)–C(9*N*), C(9*N*)–C(10*N*) and C(10*N*)–C(5*N*) bonds linking the two sulfur atoms are longest [av. 1·431 (2) Å]. The average length of the remaining C(2*N*)–C(3*N*), C(4*N*)–C(10*N*), C(6*N*)–C(7*N*) and C(8*N*)–C(9*N*) bonds is 1·402 (8) Å. This tendency is in contrast to that found in 1,5-difluoronaphthalene where the five bonds around C(9*N*) and C(10*N*) are essentially equal, with average value 1·413 (3) Å (Merresse, Courseille, Leroy & Chanh, 1975). In naphthalene, the bond distances C(1*N*)–C(2*N*) and C(2*N*)–C(3*N*) are 1·378 (2) and 1·415 (2) Å, respectively, while the five bond lengths around C(9*N*) and C(10*N*) are identical, 1·426 (2) Å (Brock & Dunitz, 1982).

The two sulfonyl groups are symmetrically arranged with respect to the naphthalene ring so that the NDS anion approximately conforms to the C_{2h} point symmetry. Each of the four O atoms directed towards the central C–C bond is rotated *ca* 60° from the plane so that the steric hindrances between the O atoms and the H atoms H(4*N*) and H(8*N*) can be minimized. The remaining two O atoms lie approximately in the plane. The O(1*N*)···H(2*N*) and O(6*N*)···H(6*N*) distances are 2·39 (6) and 2·34 (6) Å, respectively, calculated after lengthening the C–H vectors to 1·08 Å. The corresponding C–H···O angles are 105 (4)° and 104 (4)°, respectively. The difference in S–O bond distances [av. 1·454 (10) Å] may reflect the quite different hydrogen-bonding patterns around the sulfonyl O atoms. The naphthalene ring is planar with a maximum deviation of 0·033 (6) Å. The two benzene rings, both of which are planar within 0·014 (5) Å, make a dihedral angle of 2·1°.

Crystal packing is mainly dominated by an extensive hydrogen-bonding scheme (Fig. 2 and Table 3). The present structure is unique compared with other crystal structures of thiamin in that it crystallizes with a noncentrosymmetric space group while all of the crystals except *N*1′-methylthiamin diiodide (Furey, Jordan, Mariam & Lalancette, 1981) occur in centrosymmetric space groups, and in that there is no direct hydrogen bond between the thiamin cations. The water molecule plays an important role in packing by forming four hydrogen bonds in a distorted tetrahedral configuration. It is well known that the acidic proton of C(2) in thiamin forms a reasonably strong hydrogen bond. In this structure, C(2) is hydrogen bonded to O(6*N*) which is above the center of the pyrimidine ring of the same thiamin cation. O(6*N*) is displaced by 2·956 (4) Å from the pyrimidine plane and the average distance from O(6*N*) to the six atoms in the ring is 3·254 (23) Å. Similar interactions have been observed in other thiamin structures and also in the structures containing a 4′-oxopyrimidine ring (Shin, Pletcher, Sax & Blank, 1979). It has been pointed out that short C–H···O contacts are likely to occur in crystal structures that contain a large number of O atoms but relatively few proton donor groups (Taylor & Kennard, 1982). In this structure, there are only six H atoms bonded to electronegative atoms [N(1′), N(4′α), O(5γ) and O(*W*)] while there are nine potential acceptors [six O atoms in the sulfonyl groups, N(3′), O(5γ) and O(*W*)]. Accordingly, there are many short C–H···O contacts, some of which may be regarded as (albeit very weak) hydrogen bonds (Table 3), while N(3′), a potential acceptor, is not hydrogen-bonded.

Partial ring stacking occurs in a pair of the thiamin cation and the NDS anion which are connected by an N(4′α)–H···O(5*N*) hydrogen bond (see Fig. 2). The distance from S(1) to the naphthalene plane is 3·566 (2) Å and the shortest interatomic contact occurs between S(1) and C(10*N*) with a separation of 3·650 (4) Å. The thiazolium ring is tilted with respect to the naphthalene ring with a dihedral angle of 11·5°, so that only the S atom makes a close contact with the naphthalene ring. C(2), C(5) and C(5α) are displaced by 3·696 (5), 3·877 (6) and 3·847 (9) Å, respectively, from the naphthalene plane. In the same pair, sulfonyl O(5*N*) is above the N(3)–C(4) bond with a displacement of 2·900 (3) Å from the thiazolium plane.

There is no direct interaction between the naphthalene rings except the edge interaction between C(2*N*) and C(6*N*) [3·561 (7) Å] of the molecules related by a unit-cell translation along the *a* axis.

The present structure is only the third molecular complex of thiamin containing a large molecular anion, the others being thiamin picrolonate dihydrate (Shin, Pletcher, Blank & Sax, 1977) and thiamin phenanthroline aqua copper complexes (Aoki & Yamazaki, 1980). Thiamin again assumes a characteristic *F* conformation even though it interacts with the large anion in a quite different mode from those previously observed, supporting the idea that the *F* conformation is the predominant form of free thiamin. This is the only crystal structure that shows involvement of the thiazolium ring in any kind of ring-stacking interaction, although the degree of overlapping is relatively small. Although the quaternary N(3) was suggested as the principal site for ring stacking if the thiazolium ring is involved in binding to the apoenzyme (Biaglow, Mieyal, Suchy & Sable, 1969), the present study shows that the S atom with a partial positive charge is the principal site. The nature of the interaction may be the HOMO–LUMO interaction as Ishida *et al.* have suggested (Ishida, Matsui, Inoue, Hirano, Yamashita, Sugiyama, Sugiura & Tomita, 1985).

Thus far, three kinds of prominent ring-stacking interactions have been observed in thiamin-related structures. These involve only the pyrimidine ring. The first is the pyrimidine–pyrimidine interaction observed in thiamin pyrophosphate (Pletcher, Blank, Wood & Sax, 1979) and Cu(thiamin)Cl_2 (Cramer, Maynard & Evangelista, 1984). The second is the pyrimidine–phenyl ring interaction observed in 2-(α-hydroxybenzyl)thiamin (Pletcher, Sax, Blank & Wood, 1977) and 2-(α-hydroxybenzyl)oxythiamin (Shin, Pletcher & Sax, 1979) which show intramolecular stacking. Truly intermolecular ring-stacking interactions between the pyrimidine ring and the other aromatic rings have been observed only in two cases, namely, thiamin picrolonate and thiamin indole-3-propionate (Ishida *et al.*, 1985). A common feature in the two structures is that the two centrosymmetrically related thiamin molecules are dimerized *via* N(4′α)–H···N(3′) hydrogen bonds. This dimerization certainly provides quite a large planar region in the unit cell, which may facilitate the ring stacking above and below the pyrimidine rings. In fact, thiamin phenanthroline aqua copper complex, in which

Table 3. *Hydrogen bonds and close contacts*

Hydrogen bonds

a	*b*	*c*	*a*–*c* (Å)	*b*–*c* (Å)	∠*abc*(°)
N(4′α)	H(4′1)	O(5*N*)	2·836 (7)	2·04 (6)	156 (6)
N(4′α)	H(4′2)	O(*W*)	2·901 (8)	2·25 (7)	148 (7)
N(1′)	H(1′)	O(2*N*^{i})	2·786 (5)	2·02 (6)	171 (6)
O(5′*y*)	H(5′*y*)	O(*W*^{ii})	2·875 (9)	2·13 (8)	126 (6)
O(*W*)	H(*W*1)	O(4*N*)	3·007 (7)	2·33 (9)	139 (8)
O(*W*)	H(*W*2)	O(4*N*^{iii})	2·736 (7)	1·81 (7)	157 (6)
C(2)	H(2)	O(6*N*^{iv})	3·111 (6)	2·14 (5)	162 (4)

Selected close contacts (less than 3·3 Å)

C(4α)	H(4α2)	O(5*N*)	3·192 (7)	2·63 (6)	121 (5)
C(35′)	H(35′1)	O(1*N*^{v})	3·208 (6)	2·50 (6)	127 (4)
C(35′)	H(35′2)	O(2*N*^{vi})	3·244 (6)	2·29 (6)	151 (4)
C(6′)	H(6′)	O(3*N*^{v})	3·280 (6)	2·51 (6)	146 (5)
N(3)		O(5*N*)	3·121 (5)		
C(4)		O(5*N*)	2·986 (6)		
N(3)		O(1*N*^{v})	3·111 (5)		
C(4)		O(1*N*^{v})	3·086 (6)		
C(4α)		O(1*N*^{v})	3·226 (7)		
C(4α)		O(3*N*^{v})	3·285 (7)		
N(1′)		O(1*N*^{v})	3·168 (5)		

Symmetry code: (none) *x*, *y*, *z*; (i) $-\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$; (ii) $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (iv) $-1+x$, *y*, *z*; (v) $-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (vi) $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$.

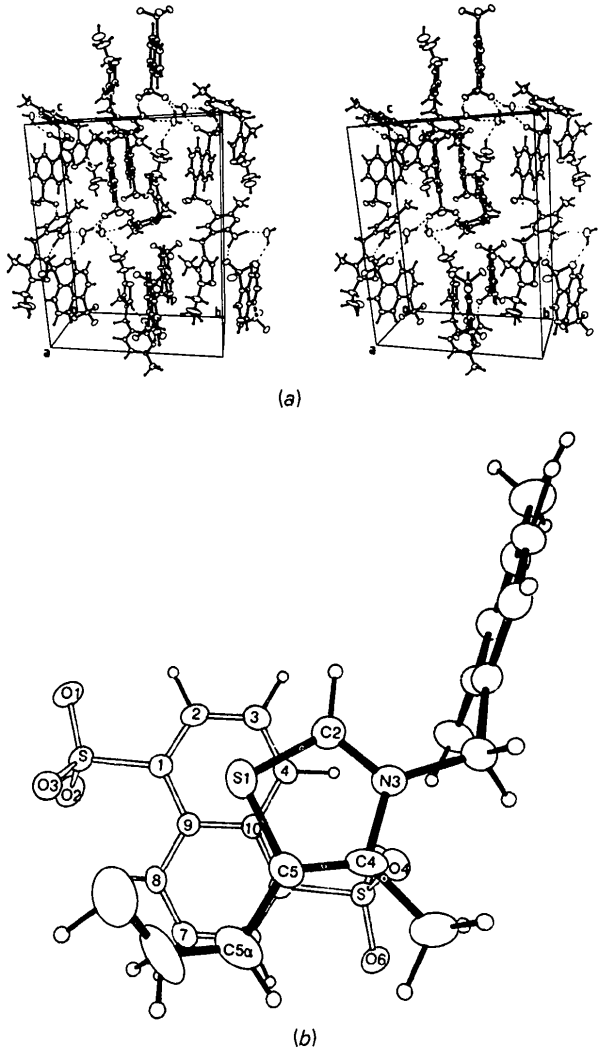

Fig. 2. (*a*) Stereoscopic view (*ORTEP*, Johnson, 1976) of the crystal packing. Dashed lines indicate the hydrogen bonds. (*b*) Perspective view (normal to the naphthalene ring) showing the partial ring stacking interaction. Thermal ellipsoids are drawn at 50% probability.

there is no such dimerization, does not show any stacking interaction between thiamin and phenanthroline. Ishida *et al.* (1985) suggested from empirical energy calculations using model compounds that the protonation of the pyrimidine makes the stacking interaction with the indole ring energetically less favorable. The fact that the deprotonated pyrimidine in thiamin picrolonate complex interacts with the aromatic ring while the protonated pyrimidine in this structure does not are consistent with this proposal. Although quite speculative, we suggest that the stacking mode in the present structure may be more significant than those involving the pyrimidine ring, from the viewpoint of the coenzyme binding mode, because the pyrimidine ring is in the protonated form and the thiamin 1,5-salt crystallizes in a noncentrosymmetric space group, thus providing a chiral packing environment which is more relevant to the environment of the apoenzyme.

We thank the Korea Science and Engineering Foundation for their support of this research.

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trans-2,3,5,6-Tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine

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(*Received* 6 *June* 1986; *accepted* 4 *August* 1986)

Abstract. $C_{14}H_{11}F_4N_3$, $M_r = 297{\cdot}3$, orthorhombic, *Pnma*, $a = 23{\cdot}102$ (2), $b = 6{\cdot}801$ (1), $c = 8{\cdot}648$ (1) Å, $V = 1358{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}45$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}085$ mm^{-1}, $F(000) = 608$, $T = 293$ K, $R = 0{\cdot}044$ for 648 reflexions [$F \geq 3\sigma(F)$]. With the exception of some methyl hydrogens each molecule is contained within the *ac* crystallographic mirror plane. Angular distortion at the azo–ring junction alleviates clashes between the azo nitrogens and ring substitutents [closest contacts: N···C(methyl) 2·75 (1) and 2·76 (1) Å; N···F 2·66 (1) and 2·68 (1) Å]. The crystal packing includes infinite intermolecular π-bonded columns of alternate trimethylphenyl and tetrafluoropyridine rings stacked at intervals of $b/2$.

Introduction. This structural determination was undertaken as part of an investigation of the mechanism for thermally converting the title compound into 1,2,4-trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*]benzo[1,2]-diazepine (Alty, Banks, Fishwick, Pritchard & Thompson, 1984). As the reaction seems likely to be initiated by hydrogen transfer from an *ortho* methyl

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