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.

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

BY R. G. PRITCHARD

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

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}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ 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$\cdots$C(methyl) $2 \cdot 75$ (1) and $2 \cdot 76$ (1) Å; N$\cdots$F $2 \cdot 66$ (1) and $2 \cdot 68$ (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

group to the azo linkage, non-bonded interactions in this region were of particular interest.

Experimental. Crystal dimensions $0.3 \times 0.3 \times 0.4$ mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, unit-cell dimensions from setting angles of 25 accurately centred reflexions ($11.5 \le \theta \le 12.5°$), $\omega–2\theta$ scan mode used to measure 1302 reflexions with ω scan width of $1.00 + 0.35 \tan\theta$ and scan speed ranging from 0.33 to $5° \text{min}^{-1}$ according to the intensity gathered in a pre-scan, $0 \le h \le 26$, $0 \le k \le 8$, $0 \le l \le 10$, $0 \le \theta \le 25°$, 648 unique structure amplitudes with $F \ge 3\sigma(F)$, negligible drift in three intensity standards ($\overline{3}30$, $\overline{3}\overline{3}4$, $\overline{4}\overline{1}1$) measured every 2 h, Lorentz and polarization corrections but absorption ignored, $MULTAN80$ (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) used to solve the phase problem, all non-hydrogen atoms found in a Fourier map, H atoms from

difference Fourier map, full-matrix least-squares refinement based on F using $SHELX76$ (Sheldrick, 1976), final $R = 0.044$, $wR = 0.045$, $w = 2.6218/[\sigma(F)^2 + 0.00007F^2]$, anisotropic thermal parameters for heavier atoms, isotropic for H. Maximum fluctuation in final difference map $\pm 0.164 \text{ e Å}^{-3}$, maximum LS shift-to-e.s.d. ratio 0.092 [U, H(71)]. Scattering factors from *International Tables for X-ray Crystallography* (1974), computation carried out on the joint CDC 7600/Amdahl 470 system of the University of Manchester Regional Computing Centre. The Cambridge Crystallographic Database was surveyed using the *Crystal Structure Search and Retrieval* (1984) interactive system accessed *via* the UMIST link to the VAX at Daresbury Laboratory.

Discussion. Fractional atomic coordinates and vibrational parameters are listed in Table 1* and bond lengths and selected angles in Table 2. The molecule, including labelling scheme, is displayed in Fig. 1 with a view of the unit cell in Fig. 2. With the exception of H(72), H(82) and H(92) all the atoms are contained within the ac mirror planes. The trimethylphenylazo dimensions show good agreement with those of 2,2′,4,4′,6,6′-hexamethylazobenzene (Gabe, Wang, Barclay & Dust, 1981) apart from the slightly longer C(1)—N(3) bond [1.442 (3) compared with 1.412 (4) Å in the title

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* Lists of structure factors, anisotropic vibrational parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43310 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
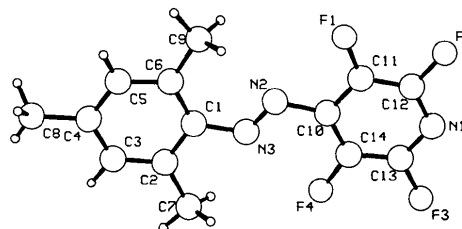
Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and vibrational parameters* $(\text{Å}^2 \times 10^4)$ *for non-hydrogen atoms*

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

	x	y	z	U_{eq}
C(1)	5705 (2)	2500	4987 (4)	531
C(2)	6217 (2)	2500	4097 (5)	620
C(3)	6737 (2)	2500	4866 (5)	721
C(4)	6773 (2)	2500	6465 (5)	708
C(5)	6261 (2)	2500	7280 (5)	738
C(6)	5719 (2)	2500	6614 (4)	583
C(7)	6212 (2)	2500	2367 (5)	931
C(8)	7352 (2)	2500	7275 (6)	1112
C(9)	5193 (2)	2500	7624 (5)	724
C(10)	4257 (2)	2500	3636 (5)	568
C(11)	3720 (2)	2500	4326 (5)	633
C(12)	3235 (2)	2500	3413 (5)	755
C(13)	3746 (2)	2500	1260 (5)	754
C(14)	4259 (2)	2500	2033 (5)	652
N(1)	3240 (2)	2500	1900 (4)	809
N(2)	4738 (1)	2500	4669 (4)	709
N(3)	5204 (1)	2500	4052 (4)	651
F(1)	3665 (1)	2500	5855 (3)	810
F(2)	2715 (1)	2500	4066 (3)	1124
F(3)	3755 (1)	2500	−289 (3)	1112
F(4)	4751 (1)	2500	1221 (3)	959

Table 2. *Bond lengths* (Å) *and selected angles* (°)

C(1)—C(2)	1.413 (5)	C(1)—C(6)	1.407 (5)
C(1)—N(3)	1.412 (4)	C(2)—C(3)	1.373 (5)
C(2)—C(7)	1.496 (6)	C(3)—C(4)	1.385 (5)
C(4)—C(5)	1.377 (6)	C(4)—C(8)	1.510 (6)
C(5)—C(6)	1.377 (6)	C(6)—C(9)	1.498 (6)
C(10)—C(11)	1.376 (5)	C(10)—C(14)	1.387 (5)
C(10)—N(2)	1.426 (5)	C(11)—C(12)	1.370 (5)
C(11)—F(1)	1.329 (4)	C(12)—N(1)	1.309 (5)
C(12)—F(2)	1.329 (4)	C(13)—C(14)	1.360 (6)
C(13)—N(1)	1.294 (5)	C(13)—F(3)	1.340 (5)
C(14)—F(4)	1.335 (4)	N(2)—N(3)	1.201 (4)
C(6)—C(1)—C(2)	121.6 (4)	N(3)—C(1)—C(2)	112.0 (3)
N(3)—C(1)—C(6)	126.4 (4)	N(2)—C(10)—C(11)	115.5 (4)
C(14)—C(10)—C(11)	115.9 (4)	N(2)—C(10)—C(14)	128.6 (4)
N(2)—C(10)—C(14)	128.6 (4)		
N(3)—N(2)—C(10)	114.8 (4)	N(2)—N(3)—C(1)	118.7 (3)

Fig. 1. Labelled view of the molecule produced with *PLUTO* (Motherwell & Clegg, 1978).
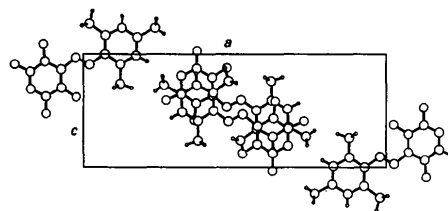

Fig. 2. Projection of the unit cell along **b**.

compound] and minor distortions from planarity at C(6) in the hexamethyl compound. Both molecules show considerable angular asymmetry at C(1), thereby alleviating the clash between C(9) and N(2), with a similar distortion at C(10) in the title molecule helping to separate N(3) and F(4) [C(9)···N(2) 2·76 (1), N(3)···F(4) 2·66 (1) Å]. The tetrafluoropyridine dimensions are unremarkable, showing good agreement with those of the corresponding azoxy compound (Banks, Farhat, Fields, Pritchard & Saleh, 1985). Like the azoxy compound there is intermolecular π interaction between alternate trimethylphenyl and tetrafluoropyridyl rings, which, in the azo case, form infinite columns parallel to **b** generated by the screw axis, $1 - x$, $\frac{1}{2} + y$, $1 - z$ [C(4)···C(12) 3·40 (1), C(6)··· C(10) 3·41 (1) Å].

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Structures of 2'-Deoxytubercidin* (I) and 2'-Deoxytubercidin Dihydrate (II)†

BY VOLKER ZABEL AND WOLFRAM SAENGER

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany

AND FRANK SEELA

Laboratorium für Organische und Bioorganische Chemie, Fachbereich Biologie/Chemie, Universität Osnabrück, Barbarastrasse 7, D-4500 Osnabrück, Federal Republic of Germany

Abstract. (I): $C_{11}H_{14}N_4O_3$, $M_r = 250·3$, orthorhombic, $P2_12_12_1$, $a = 10·667$ (3), $b = 14·997$ (4), $c = 7·158$ (2) Å, $V = 1145·1$ Å^3, $Z = 4$, $D_x = 1·452$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 0·87$ mm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 2·7\%$ for 1132 observed reflections. (II): $C_{11}H_{14}N_4O_3.2H_2O$, $M_r = 286·3$, orthorhombic, $P2_12_12_1$, $a = 9·676$ (2), $b = 20·221$ (5), $c = 6·933$ (2) Å, $V = 1356·5$ Å^3, $Z = 4$, $D_x = 1·402$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 0·90$ mm^{-1}, $F(000) = 608$, $T = 295$ K, $R = 4·7\%$ for 1318 observed reflections. The bond parameters of the two compounds are almost identical. Although the packing in the crystals of (I) and (II) is different, the conformations of the two molecules are comparable and similar to that observed in crystalline tubercidin [Abola & Sundaralingam (1973). *Acta Cryst.* B**29**, 697–703]. In (I) the sugar and base moieties form layers which are held together by hydrogen bonding, but with no parallel stacking of the bases. Parallel stacking of the bases occurs in (II) with a base–base separation of $c/2 = 3·46$ Å. The stacks are separated in the **a** direction by the two water molecules and in the [010] direction by sugar residues. Owing to the additional water molecules, the hydrogen-bonding scheme in (II) is more complex than in (I).

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* 7-(2'-Deoxy-β-D-*erythro*-pentofuranosyl)-7*H*-pyrrolo[2,3-*d*]-pyrimidin-4-amine.
† Dedicated to Professor Georg Manecke on the occasion of his 70th birthday.

Introduction. Compared with double-helical DNA, the alternating polynucleotide copolymer poly-d(AT) exhibits some unusual physical properties (Schefler,