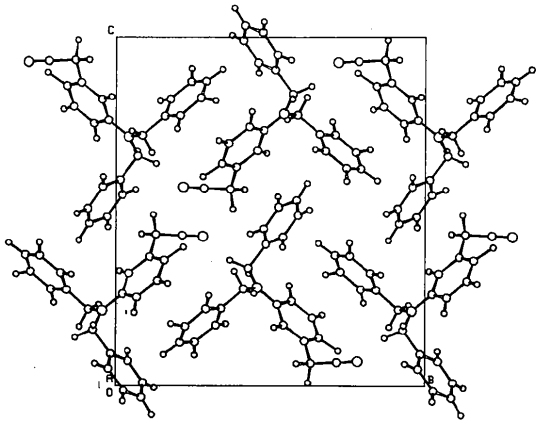

Fig. 3. Packing of the molecules in the unit cell.

being 95.7 (1) and 85.5 (1)° for the C2–C7 and C9–C14 phenyl rings, respectively. No particular trend is observed for the C—C distances in these two rings, while the endocyclic angles at the *ipso* and *meta* C atoms decrease by approximately the same magnitude as those at the *ortho* and *para* C atoms increase. These angular deformations are due to the effect exerted by the amino substitutent, which is in agreement with the findings of Domenicano, Vaciago & Coulson (1975).

The acetonitrile group is linear [CH_2—C≡N = 179.8 (4)°] and is tilted with respect to the benzene plane by 59.1 (1)°, no electronic effect being present to impose any particular orientation. Fig. 3 shows how the molecules are packed in the unit cell under van der Waals interactions.

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Structure of Amprolium Hydrochloride

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Abstract. 1-[(4-Amino-2-propyl-5-pyrimidinyl)-methyl]-2-methylpyridinium chloride hydrochloride, $C_{14}H_{19}N_4^+.Cl^-.HCl$, $M_r = 315.2$, triclinic, $P\bar{1}$, $a = 11.327$ (2), $b = 13.842$ (2), $c = 10.959$ (2) Å, $\alpha = 90.68$ (2), $\beta = 110.13$ (1), $\gamma = 99.10$ (2)°, $V = 1588.9$ (4) Å^3, $Z = 4$, $D_x = 1.318$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 35.7$ cm^{-1}, $F(000) = 664$, $T = 297$ K, $R = 0.054$ for 3680 reflections with $F \geq 6\sigma(F)$. The two independent divalent amprolium molecular ions are interconnected by four N(4′α)—H···Cl$^-$ (amino group) hydrogen bonds forming a dimeric unit which has a pseudo center of symmetry, discounting the propyl side chains. There are only van der Waals interactions between these dimeric units.

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The conformation of amprolium is very similar to the *F* form of thiamin in that an H atom sits on top of the pyrimidine ring.

Introduction. Thiamin (vitamin B_1), in the form of pyrophosphate ester, is a coenzyme in a number of enzyme systems that catalyze the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups. Although the Breslow mechanism depicts the essential features of thiamin catalysis, many details of the enzymatic reaction, such as the role of the 4′-amino group and the binding mode of the coenzyme, have yet to be elucidated (Kluger, 1987). Knowledge of the structural characteristics of the antagonists of thiamin may help in understanding some aspects of these problems. There are two major types of potent thiamin antagonists: oxythiamin has an intact thiazolium ring but contains a 4′-oxopyrimidine instead of a 4′-aminopyrimidine moiety, while the other antagonists, pyrithiamin and amprolium, have the 4′-aminopyrimidine moiety but contain a pyridine moiety instead of the thiazolium ring and thus lack the active site. The former acts as an inhibitor to thiamin pyrophosphate-requiring enzymes while the latter inhibit thiamin kinase which is involved in thiamin transport (Rogers, 1970). X-ray analyses revealed that oxythiamin assumes the *V* conformation which is different from the characteristic *F* or *S* form of thiamin (Shin, Pletcher, Sax & Blank, 1979; Shin, Pletcher & Sax, 1981). The crystal structure of pyrithiamin has not been reported and our efforts to obtain a crystal have, thus far, been in vain. Instead we obtained the crystal of amprolium, which is conformationally homologous to pyrithiamin and used as a poultry coccidiostat, and determined its crystal structure.

Experimental. Colorless plate-like crystals obtained from a methanol solution by slow evaporation; crystal *ca* 0.3 × 0.2 × 0.2 mm; Rigaku AFC diffractometer; graphite-monochromated Cu $K\alpha$ radiation; $2\theta \le 120°$, ω-2θ scan, scan speed 2° min^{-1} in 2θ, ω-scan width $(1.5 + 0.5\tan\theta)°$; background measured for 10 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values for 25 centered reflections with $25 \le 2\theta \le 60°$; intensity checks for three standard reflections showed little (±3%) variations; 4733 independent reflections (h 0 to 12, k −15 to 15, l −12 to 12), 3680 (77.8%) observed with $F \ge 6\sigma(F)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods and refined by full-matrix least squares on *F* with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976); H atoms identified in the 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 ($k = 1.00$, $g = 0.00384$); $wR = 0.061$ for 3680 observed reflections, 521 variables, $R = 0.081$ and $wR = 0.065$ for all data, $S = 1.173$, $(\Delta/\sigma)_{max} = 0.20$ [U_{11} of H(4′α*B*)] in final refinement cycle; max. and min. heights in final difference map 0.42 and −0.76 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 1. *Atomic coordinates* (× 10^4) *and thermal parameters* (Å^2)

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

	x	*y*	*z*	U_{eq}
Molecule *A*				
N(1)	4321 (2)	1863 (2)	1686 (2)	0.023
C(2)	3139 (3)	1310 (2)	1307 (3)	0.030
C(3)	2529 (3)	1194 (3)	2206 (4)	0.042
C(4)	3114 (4)	1592 (3)	3452 (4)	0.051
C(5)	4331 (4)	2124 (3)	3825 (4)	0.047
C(6)	4923 (3)	2262 (2)	2912 (3)	0.033
C(2α)	2546 (4)	855 (3)	−41 (4)	0.046
C(1,5′)	4960 (3)	2004 (2)	693 (3)	0.026
N(1′)	7405 (3)	4262 (2)	1309 (3)	0.033
C(2′)	8495 (3)	3916 (2)	1803 (3)	0.031
N(3′)	8533 (2)	2988 (2)	1994 (3)	0.033
C(4′)	7410 (3)	2361 (2)	1727 (3)	0.027
C(5′)	6218 (3)	2684 (2)	1154 (3)	0.026
C(6′)	6266 (3)	3646 (2)	964 (3)	0.031
C(2′α)	9709 (4)	4654 (3)	2134 (5)	0.048
C(2′β)	10689 (4)	4364 (3)	1557 (5)	0.055
C(2′γ)	11477 (4)	3648 (4)	2325 (5)	0.059
N(4′α)	7482 (3)	1438 (2)	1983 (3)	0.036
Molecule *B*				
N(1)	10743 (2)	8168 (2)	3224 (2)	0.026
C(2)	11937 (3)	8660 (2)	3422 (4)	0.039
C(3)	12346 (4)	8736 (3)	2366 (6)	0.063
C(4)	11545 (6)	8354 (3)	1145 (6)	0.074
C(5)	10337 (5)	7872 (3)	971 (5)	0.061
C(6)	9960 (3)	7782 (2)	2042 (3)	0.037
C(2α)	12751 (4)	9103 (4)	4747 (5)	0.062
C(1,5′)	10308 (3)	8079 (2)	4375 (3)	0.027
N(1′)	7808 (3)	5926 (2)	4127 (3)	0.036
C(2′)	6740 (3)	6315 (3)	3767 (4)	0.040
N(3′)	6734 (2)	7239 (2)	3547 (3)	0.037
C(4′)	7861 (3)	7824 (2)	3649 (3)	0.027
C(5′)	9036 (3)	7461 (2)	4098 (3)	0.026
C(6′)	8944 (3)	6493 (2)	4311 (3)	0.032
C(2′α)	5517 (4)	5648 (3)	3651 (5)	0.069
C(2′β)	4448 (5)	5684 (4)	2412 (6)	0.087
C(2′γ)	3718 (5)	6517 (4)	2342 (6)	0.077
N(4′α)	7784 (3)	8730 (2)	3341 (3)	0.032
Cl(1)	7078 (1)	6313 (1)	543 (1)	0.042
Cl(2)	7797 (1)	3790 (1)	4762 (1)	0.040
Cl(3)	5277 (1)	9675 (1)	2007 (1)	0.038
Cl(4)	9942 (1)	431 (1)	3114 (1)	0.035

Discussion. Final atomic parameters are listed in Table 1.* An *ORTEP*II (Johnson, 1976) view of the asymmetric unit with the atomic numbering scheme is presented in Fig. 1. Bond distances and angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms and the molecular dimensions involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55546 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1002]

Table 2. *Bond distances* (Å), *bond angles* (°) *and intermolecular hydrogen-bond geometry* (Å, °)

	Molecule *A*	Molecule *B*
N(1)—C(2)	1.355 (4)	1.358 (4)
N(1)—C(6)	1.345 (4)	1.339 (4)
N(1)—C(1,5′)	1.500 (4)	1.504 (4)
C(2)—C(3)	1.382 (5)	1.386 (6)
C(2)—C(2α)	1.480 (5)	1.488 (6)
C(3)—C(4)	1.361 (6)	1.374 (8)
C(4)—C(5)	1.376 (6)	1.372 (8)
C(5)—C(6)	1.383 (5)	1.381 (6)
C(1,5′)—C(5′)	1.497 (4)	1.484 (4)
N(1′)—C(2′)	1.334 (4)	1.339 (4)
N(1′)—C(6′)	1.358 (4)	1.346 (4)
C(2′)—N(3′)	1.309 (4)	1.305 (5)
C(2′)—C(2′α)	1.507 (5)	1.503 (5)
N(3′)—C(4′)	1.358 (4)	1.368 (4)
C(4′)—C(5′)	1.425 (4)	1.426 (4)
C(4′)—N(4′α)	1.320 (4)	1.311 (4)
C(5′)—C(6′)	1.346 (4)	1.357 (4)
C(2′α)—C(2′β)	1.553 (6)	1.484 (7)
C(2′β)—C(2′γ)	1.507 (6)	1.510 (8)
C(3)—C(2)—N(1)	118.2 (3)	118.1 (4)
C(4)—C(3)—C(2)	121.1 (3)	120.7 (4)
C(5)—C(4)—C(3)	119.6 (4)	119.8 (5)
C(5)—C(6)—N(1)	120.1 (3)	121.1 (3)
C(6)—N(1)—C(2)	121.9 (2)	121.6 (3)
C(6)—C(5)—C(4)	119.1 (4)	118.5 (5)
C(2α)—C(2)—N(1)	119.5 (3)	119.4 (3)
C(2α)—C(2)—C(3)	122.4 (3)	122.5 (3)
C(1,5′)—N(1)—C(2)	117.7 (2)	118.0 (3)
C(1,5′)—N(1)—C(6)	120.4 (2)	120.4 (2)
N(3′)—C(2′)—N(1′)	122.9 (3)	122.7 (3)
C(4′)—N(3′)—C(2′)	118.2 (3)	118.4 (3)
C(4′)—C(5′)—C(1,5′)	123.4 (2)	124.1 (2)
C(5′)—C(1,5′)—N(1)	114.5 (2)	114.5 (2)
C(5′)—C(4′)—N(3′)	121.2 (3)	121.1 (3)
C(5′)—C(6′)—N(1′)	120.6 (3)	121.3 (3)
C(6′)—N(1′)—C(2′)	120.4 (3)	120.4 (3)
C(6′)—C(5′)—C(1,5′)	119.9 (3)	120.1 (3)
C(6′)—C(5′)—C(4′)	116.6 (3)	115.8 (3)
C(2′α)—C(2′)—N(1′)	116.4 (3)	117.4 (3)
C(2′α)—C(2′)—N(3′)	120.7 (3)	119.9 (3)
C(2′β)—C(2′α)—C(2′)	114.4 (3)	114.4 (4)
C(2′γ)—C(2′β)—C(2′α)	114.1 (4)	116.2 (5)
N(4′α)—C(4′)—N(3′)	116.7 (3)	115.7 (3)
N(4′α)—C(4′)—C(5′)	122.1 (3)	123.2 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(1′A)—H···Cl(1)	0.77 (4)	2.25 (4)	3.013 (3)	174 (4)
N(4′αA)—H(1)···Cl(3)	0.85 (4)	2.37 (4)	3.211 (3)	171 (4)
N(4′αA)—H(2)···Cl(4)	0.85 (5)	2.37 (5)	3.184 (3)	160 (4)
N(1′B)—H···Cl(2)	0.83 (3)	2.22 (3)	3.045 (3)	172 (3)
N(4′αB)—H(1)···Cl(4)	0.85 (4)	2.35 (4)	3.193 (3)	172 (4)
N(4′αB)—H(2)···Cl(3)	0.89 (4)	2.33 (4)	3.205 (3)	165 (4)

Crystal packing (Fig. 2) is exceptionally simple for compounds containing the 4′α-aminopyrimidine ring. The two independent divalent amprolium molecular ions are interconnected by four N(4′α)—H···Cl^- hydrogen bonds (Table 2) involving two independent Cl^- ions to form a dimeric unit. The other two Cl^- ions are hydrogen bonded to the two N(1′) atoms. There is a pseudo center of symmetry at (0.75, 0.50, 0.25) in the dimeric unit, discounting the propyl side chains. There are only van der Waals interactions between these dimeric units.

Molecular dimensions of the two independent molecules agree well within experimental e.s.d.'s. N(1′) is the protonation site as in the case of thiamin. Bond distances within the protonated pyrimidine moieties are in good agreement with those in protonated thiamin, showing the typical quinonoid structure in which the C(2′)—N(3′), C(5′)—C(6′) and C(4′)—N(4′α) bonds become short. The pyrimidine and pyridine rings are planar with maximum deviations of 0.027 (3) and 0.015 (3) Å for molecule *A* and 0.033 (3) and 0.015 (4) Å for molecule *B*, respectively.

The conformation of amprolium is very similar to the *F* form of thiamin in that an H atom sits on top of the pyrimidine ring. The torsion angles C(6)—N(1)—C(1,5′)—C(5′) and N(1)—C(1,5′)—C(5′)—C(4′), which correspond to φ_T and φ_P of thiamin (Shin, Pletcher, Blank & Sax, 1977), are −5.6 and 92.5° for molecule *A* and −5.8 and 89.1° for molecule *B*, respectively; $\varphi_T \simeq 0$ and $\varphi_P \simeq \pm 90°$ for thiamin in the *F* form. It has been proposed that preference for the *F* form of thiamin may originate from

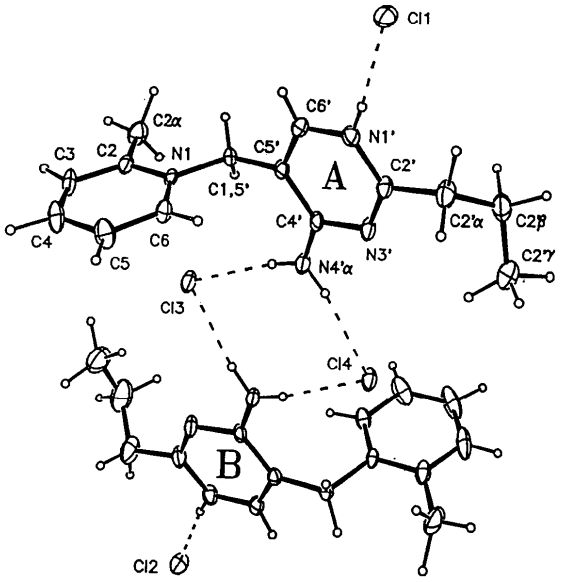

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the asymmetric unit of amprolium hydrochloride with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The dotted lines denote the hydrogen bonds.

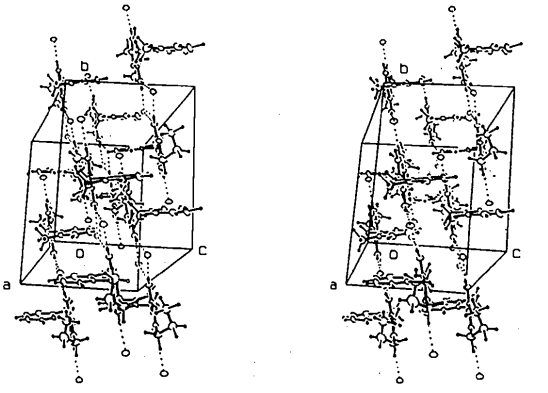

Fig. 2. Stereoscopic *ORTEP*II packing drawing. The dotted lines denote the hydrogen bonds.

the favorable interaction between the acidic C(2) proton of the thiazolium ring and the π electrons in the pyrimidine ring (Turano, Pletcher, Furey & Sax, 1982). In this context, the present conformation is a rather unexpected one since amprolium apparently does not have an acidic proton in the pyridine ring and thus could adopt the less observed *S* form ($\varphi_T \simeq$ 110 and $\varphi_P \simeq \pm 180°$) of thiamin in which H(6′) sits on top of the thiazolium ring.

It has been pointed out that the relative orientation of the two rings in the thiamin-related molecules is determined mainly by the interactions between the substituents at the four positions [C(2), C(6), C(4′) and C(6′) in amprolium] which are *ortho* to the methylene bridge C atom (Shin & Kim, 1986). Since amprolium and pyrithiamin have the same substituents at these positions, we expect that the conformational property of pyrithiamin may be similar to that of amprolium. Together with the presence of the pyridine ring, which is positively charged like the thiazolium ring but lacking the active site, conformational similarity may be the major factor for the inhibitory power of amprolium and pyrithiamin.

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Molecular Co-crystals of Carboxylic Acids. 10.* Structure of the 1:1 Adduct of Triphenylphosphine Oxide with (Pentachlorophenoxy)acetic Acid

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Abstract. $C_{18}H_{15}OP.C_8H_3Cl_5O_3$, $M_r = 602.7$, triclinic, $P\bar{1}$, $a = 10.185$ (6), $b = 12.036$ (5), $c = 12.194$ (6) Å, $\alpha = 92.21$ (3), $\beta = 108.48$ (3), $\gamma = 106.10$ (3)°, $V = 1349$ (1) Å^3, $Z = 2$, $D_x = 1.483$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.63$ mm^{-1}, $F(000) = 612$, $T = 295$ K, $R = 0.041$ for 3317 observed reflections. The compound was prepared by interacting a 1:1 molar ratio of triphenylphosphine oxide and (pentachlorophenoxy)acetic acid in toluene/ethanol and allowing the mixture to evaporate to dryness. The two organic molecules associate through a single directed hydrogen bond between the carboxylic acid group and the phosphoryl O atom [OH···O 2.541 (4) Å].

Introduction. Triphenylphosphine oxide (TPPO) has been reported as a useful crystallizing aid (Etter & Baures, 1988). This is possible because the molecule is a good acceptor, available for hydrogen-bonding interactions through the phosphoryl O atom, with examples of both O—H and N—H donor-molecule adducts already reported. The conformational flexibility of the TPPO molecule *via* rotation of the three phenyl rings about the C—P bonds makes it ideal for the stabilization of crystal lattices. Interesting comparisons can therefore be made both with the parent molecule (Spek, 1987; Ruban & Zabel, 1976;

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