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Structure of 3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium Chloride

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Abstract. $C_{13}H_{16}NOS^+.Cl^-$, $M_r = 269.79$, triclinic, $P\bar{1}$, $a = 6.954$ (1), $b = 9.049$ (1), $c = 11.541$ (2) Å, $\alpha = 73.87$ (1), $\beta = 74.47$ (1), $\gamma = 87.79$ (1)°, $V = 671.7$ (1) Å^3, $Z = 2$, $D_x = 1.334$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 38.5$ cm^{-1}, $F(000) = 284$, $T = 295$ K, $R = 0.046$ for 1742 reflections with $I \geq 2\sigma(I)$. The title compound, which is an antagonist of thiamin, assumes a conformation similar to the S form of thiamin. There are close S···Cl$^-$ electrostatic interactions [3.197 (1) Å] and a weak C(2)—H···Cl$^-$ hydrogen bond [3.421 (3) Å] as frequently observed in thiamin.

Introduction. The title compound (benzylthiamin) is an antagonist of thiamin (vitamin B$_1$) in which the 4-amino-2-methylpyrimidine ring is replaced by a phenyl ring. Benzylthiamin does not show any activity owing to the absence of the pyrimidine moiety which is essential for the activity of thiamin, although its function inside the protein is not clearly understood (Schellenberger, 1982). The crystal structure of N-benzyl-4-methylthiazolium bromide, which is homologous to benzylthiamin but devoid of the 5-(2-hydroxyethyl) side chain, has been determined

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(Power, Pletcher & Sax, 1970). Its conformation is similar to the S form of thiamin which is less frequently observed than the F form. In a continuing study of the conformational characteristics of thiamin analogs, we have determined the crystal structure of benzylthiamin.

Experimental. Transparent plate-shaped crystals of benzylthiamin (Aldrich Chemical Co.) obtained from a CHCl$_3$/toluene (1:1 v/v) solution by slow evaporation; crystal size ca 0.2 × 0.3 × 0.4 mm; Rigaku AFC diffractometer; graphite-monochromated Cu $K\alpha$ radiation; $2\theta \leq 120°$; ω–2θ scan, scan speed 2° min^{-1} in 2θ, ω-scan width $(1.7 + 0.1\tan\theta)°$; 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 $25 \leq 2\theta \leq 50°$; intensity checks for three standard reflections showed little random variation $(\pm 1\%)$; 1997 independent reflections (h 0 to 7, k −10 to 10, l −11 to 12), 1742 (87%) observed with $I \geq 2\sigma(I)$ 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 SHELX76 (Sheldrick, 1976); H atoms identified in the

difference map and refined isotropically; $\Sigma w(|F_o| - |F_c|)^2$ 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 ($k = 1.000$, $g = 0.00381$); $wR = 0.045$ for 1742 observed reflections, 218 variables, $R = 0.057$ and $wR = 0.053$ for all data, $S = 0.933$, $(\Delta/\sigma)_{max} = 0.227$ [x of H(5γ)] in final refinement cycle; max. and min. heights in final difference map 0.27 and -0.44 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are listed in Table 1.* An *ORTEP* (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.

The molecular dimensions of the thiazolium moiety agree very well with those of thiamin. The thiazolium and phenyl rings are planar with maximum deviations of 0.010 and 0.007 Å, respectively. The methylene bridge atom C(35′) deviates by 0.020 (3) and 0.050 (3) Å from these two planes which make a dihedral angle of 86.2°. The torsion angles C(2)—N(3)—C(35′)—C(5′) and N(3)—C(35′)—C(5′)—C(4′), which define the relative orientation of the two aromatic rings and correspond to φ_T and φ_P in thiamin, are 110.1 (3) and 146.4 (4)°, respectively, in benzylthiamin. These angles in *N*-benzyl-4-methylthiazolium bromide are 103.8 (4) and 126.3 (5)°, which are comparable to those of thiamin in the *S* conformation (Shin, Pletcher, Blank & Sax, 1977). While free thiamin overwhelmingly assumes the *F* conformation (25 cases), there are six cases of free thiamin occurring in the *S* conformation which are clustered around $\varphi_T \simeq \pm 110$ and $\varphi_P \simeq \pm 130°$. Thiamin analogs with a bulky substituent at C(2) assume the *S* conformation with $\varphi_T \simeq \pm 90$ and $\varphi_P \simeq 180°$. It has been proposed that preference for the *F* conformation over the other conformations in free thiamin may originate from the favorable interaction of the acidic C(2) proton and the π electrons in the pyrimidine ring of thiamin (Turano, Pletcher, Furey & Sax, 1982). It is interesting to note that both *N*-benzyl derivatives assume the *S* conformation despite the fact that they still have the acidic C(2) proton. In most thiamin structures, the C(2) atom forms a hydrogen bond with the negatively charged species and there are close contacts between S(1) and either O(5γ) and/or a halogen ion due to the partial

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

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

	x	y	z	U_{eq}
Cl	949 (1)	7149 (1)	8624 (1)	0.044
S(1)	3197 (1)	7298 (1)	672 (1)	0.039
C(2)	2793 (4)	5379 (3)	1093 (2)	0.037
N(3)	3696 (3)	4657 (2)	1952 (2)	0.033
C(4)	4760 (4)	5635 (3)	2322 (2)	0.033
C(4α)	5909 (5)	4998 (4)	3262 (3)	0.049
C(5)	4612 (4)	7129 (3)	1714 (2)	0.036
C(5α)	5608 (4)	8525 (3)	1804 (3)	0.042
C(5β)	7690 (4)	8841 (4)	932 (3)	0.046
O(5γ)	7612 (3)	9119 (3)	-317 (2)	0.050
C(35′)	3530 (4)	2966 (3)	2477 (3)	0.038
C(1′)	-455 (6)	2691 (5)	5512 (4)	0.070
C(2′)	64 (6)	1393 (4)	6284 (3)	0.061
C(3′)	1678 (6)	613 (4)	5845 (3)	0.063
C(4′)	2816 (5)	1150 (4)	4613 (3)	0.050
C(5′)	2321 (4)	2460 (3)	3815 (2)	0.036
C(6′)	652 (5)	3220 (4)	4280 (3)	0.052

Table 2. *Bond distances* (Å) *and angles* (°)

|				
S(1)—C(2)	1.681 (3)	S(1)—C(5)	1.720 (3)	
C(2)—N(3)	1.321 (3)	N(3)—C(4)	1.394 (3)	
N(3)—C(35′)	1.477 (3)	C(4)—C(4α)	1.493 (4)	
C(4)—C(5)	1.353 (3)	C(5)—C(5α)	1.505 (4)	
C(5α)—C(5β)	1.511 (4)	C(5β)—O(5γ)	1.408 (4)	
C(35′)—C(5′)	1.498 (4)	C(1′)—C(2′)	1.364 (5)	
C(1′)—C(6′)	1.381 (5)	C(2′)—C(3′)	1.359 (5)	
C(3′)—C(4′)	1.388 (5)	C(4′)—C(5′)	1.380 (4)	
C(5′)—C(6′)	1.385 (4)			
N(3)—C(2)—S(1)	112.4 (2)	C(4)—N(3)—C(2)	113.9 (2)	
C(4)—C(5)—S(1)	111.1 (2)	C(4α)—C(4)—N(3)	120.6 (2)	
C(5)—S(1)—C(2)	91.1 (1)	C(5)—C(4)—N(3)	111.6 (2)	
C(5)—C(4)—C(4α)	127.8 (3)	C(5α)—C(5)—S(1)	120.8 (2)	
C(5α)—C(5)—C(4)	128.0 (2)	C(5β)—C(5α)—C(5)	111.8 (2)	
O(5γ)—C(5β)—C(5α)	110.0 (2)	C(35′)—N(3)—C(2)	122.0 (2)	
C(35′)—N(3)—C(4)	124.1 (2)	C(3′)—C(2′)—C(1′)	120.2 (3)	
C(4′)—C(3′)—C(2′)	119.9 (3)	C(4′)—C(5′)—C(35′)	119.5 (2)	
C(5′)—C(35′)—N(3)	113.1 (2)	C(5′)—C(4′)—C(3′)	121.0 (3)	
C(5′)—C(6′)—C(1′)	120.7 (3)	C(6′)—C(1′)—C(2′)	120.3 (4)	
C(6′)—C(5′)—C(35′)	122.5 (2)	C(6′)—C(5′)—C(4′)	118.0 (2)	
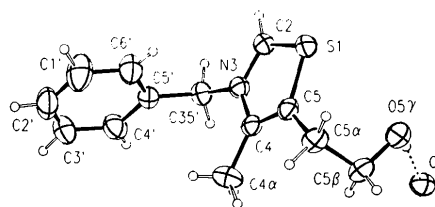
Fig. 1. *ORTEP* (Johnson, 1976) drawing of benzylthiamin with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. The dotted line denotes the hydrogen bond.

positive charge on S(1) (Sax, Pulsinelli & Pletcher, 1974). Benzylthiamin also has a close S···Cl$^-$ electrostatic interaction [S(1)···Cl$^-$(x, y, $-1 + z$) 3.197 (1) Å, 0.65 Å shorter than the sum of the van der Waals radii, 3.85 Å] and a weak C(2)—H···Cl$^-$ hydrogen bond [C(2)···Cl$^-$ 3.421 (3), H(2)···Cl$^-$ 2.61 (3) Å, C(2)—H(2)···Cl$^-$ 143 (3)°]. The distance between S(1) and O(5γ) is 3.303 (2) Å, which is
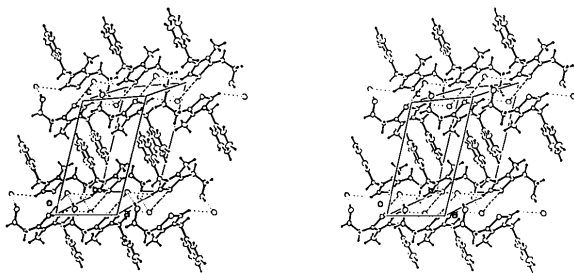
Fig. 2. Stereoscopic *ORTEP* packing drawing. The dotted and dashed lines denote the hydrogen bonds and electrostatic interactions, respectively.

slightly larger than the sum of van der Waals radii (3.25 Å). The conformation of the hydroxyethyl side chain is similar to that found in thiamin compounds with a close S···O interaction: $\varphi_{5\alpha}$ = S(1)—C(5)—C(5α)—C(5β) = 90.5 and $\varphi_{5\beta}$ = C(5)—C(5α)—C(5β)—O(5γ) = − 60.8°.

The chloride ions play an important role in the crystal packing (Fig. 2). Besides the C(2)—H···Cl⁻ hydrogen bond and the S(1)···Cl⁻ electrostatic interaction, the Cl⁻ ion is hydrogen bonded to O(5γ) [O(5γ)···Cl⁻ 3.071 (2), H(5γ)···Cl⁻ 2.30 (4) Å,

O(5γ)—H(5γ)···Cl⁻ 175 (4)°]. Two molecules related by a center of symmetry at ($\frac{1}{2},\frac{1}{2}$,0) are dimerized *via* a pair of the C(2)—H···Cl⁻···H—O(5γ) hydrogen-bonding chains. These dimers are linked by strong S(1)···Cl⁻ electrostatic interactions to form a molecular chain along the *a* axis. There are only van der Waals interactions between the molecular chains.

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Structure of a Chalcone

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Abstract. 1-(7-Hydroxy-2,2-dimethylchroman-6-yl)-3-phenyl-2-propen-1-one, $C_{20}H_{20}O_3$, M_r = 308.38, $P2_1/a$, *a* = 12.002 (2), *b* = 11.013 (2), *c* = 12.652 (3) Å, β = 106.24 (3)°, *V* = 1605.6 Å³, *Z* = 4, D_m = 1.26 (2), D_x = 1.275 Mg m⁻³, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.079 mm⁻¹, *F*(000) = 656, *T* = 293 K, *R* = 0.037, *wR* = 0.034 for 892 reflections with $I > 3\sigma(I)$. There is an internal hydrogen bond O—H···O between the carbonyl O atom in the cinna-

moyl group and the hydroxy group of the chroman moiety. The conformational analysis shows that the phenyl ring is *trans* with respect to the double bond linking it with the chroman group. The pyran ring is in the prevalent half-chair conformation.

Introduction. Analytical studies have shown that chalcones are the precursors of isoflavones, which are the pigments of many plants. The title compound, 6-cinnamoyl-7-hydroxy-2,2-dimethylchroman, which is a chalcone, was prepared by treating

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