monohydrate (Pletcher, Sax, Sengupta, Chu & Yoo, 1972), the nitrate salt is anhydrous (Ishida, Tanaka & Inoue, 1984).

The cation and atomic numbering are shown in Fig. 1. The dihedral angle between the pyrimidine and thiazolium ring planes is 84·5 (8)° which falls within the range (70·9 to 104·0°) observed in various thiamin derivatives. The value for the chloride salt is 77·2° and for the nitrate 84·7°. The thiamin cation has the *F* conformation as defined by Pletcher, Sax, Turano & Chang (1982). The torsion angles are φ_T = 2·3 (8), φ_P = 83·2 (7), $\varphi_{5\alpha}$ = 17·8 (8) and $\varphi_{5\beta}$ = 54·3°. The φ_T and φ_P angles are appropriate for the *F* conformation. The $\varphi_{5\alpha}$ value deviates significantly from the average value of 76·4° given by Pletcher *et al.* (1982). A somewhat similar situation was observed in the nitrate salt (Ishida *et al.*, 1984), where φ_T of 5·9 (5), φ_P of 83·1 (4), and $\varphi_{5\alpha}$ of −92·8 (4)° were appropriate for the *F* conformation but the $\varphi_{5\beta}$ value of 175·7 (3)° was significantly different from 70°. Since in the perchlorate, the nitrate, and the chloride salts, the hydroxyethyl side chain is involved in hydrogen bonding, the conformation of this side chain probably reflects crystal-packing requirements. Consequently, average values for the $\varphi_{5\alpha}$ and $\varphi_{5\beta}$ torsion angles are meaningless.

The distances in the thiamin cation are similar to those of the 29 other thiamin derivatives found in the Cambridge Structural Database (1986). The S(1)—C(5) distance of 1·732 (7) Å is always longer than S(1)—C(2) of 1·686 (7) Å. C(4)—C(5), 1·332 (9) Å, is essentially a localized double bond. The bonds involving N(3) in the ring, N(3)—C(2) of 1·311 (8) Å and N(3)—C(4) of 1·401 (8) Å, show some delocalization while the N(3)—C(10) bond of 1·486 (8) Å is in essence a single bond. In summary, there is very little delocalization in the thiazolium ring. The distances in the pyrimidine ring are also close to the average values.

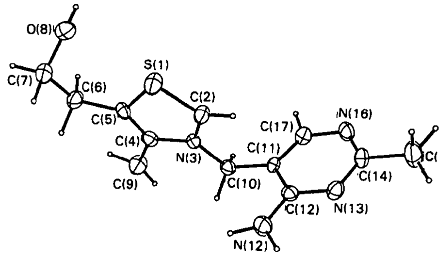

Fig. 1. A view of the thiaminium cation showing the atomic numbering and the thermal ellipsoids.

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Structure of 2-(2,3-Dihydro-1,3-dimethylbenzimidazol-2-yl)phenol

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Abstract. $C_{15}H_{16}N_2O$, M_r = 240·31, monoclinic, $P2_1/c$, a = 8·853 (3), b = 10·731 (3), c = 13·729 (4) Å, β = 94·81 (3)°, V = 1299·7 Å³, Z = 4, D_x = 1·228 Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å (graphite monochromator), μ(Mo $K\alpha$) = 0·073 mm^{-1}, F(000) = 512, T = 295 K, final R = 0·032 for 1352 nonzero reflections. The five-membered ring assumes an envelope conformation in which the N lone pairs and

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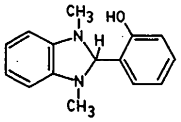
the intervening C—H bond are antiperiplanar. The mean plane of the hydroxyphenyl group is approximately perpendicular to the other aromatic ring, and the phenolic hydroxy is strongly H-bonded intramolecularly to an N atom.

Introduction. We are interested in the design and synthesis of reducing agents that have some of the features of redox enzymes, including a site that acts as a donor of hydride and an adjacent site that recognizes and binds reducible substrates (Ramos, Tarazi & Wuest, 1987; Bachand, Ramos & Wuest, 1987). A simple compound that incorporates these features is the title compound (1), prepared by the condensation of salicylaldehyde with *N,N'*-dimethyl-1,2-benzenediamine (El'tsov & Muravich-Aleksandr, 1965). Compound (1) contains a C—H bond activated as a donor of hydride by two adjacent N lone pairs, as well as a hydroxy group that can serve as a point of attachment for reducible substrates. The structure of (1) has been determined by the X-ray crystallographic study summarized below.



(1)

Table 1. *Refined coordinates* (×10⁴, H ×10³) *and equivalent isotropic temperature factors* (Å²×10³)

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

	x	y	z	U_{eq}*
O(2')	2473 (2)	1389 (1)	3385 (1)	55
N(1)	2056 (1)	1313 (1)	997 (1)	43
N(3)	460 (1)	395 (1)	2005 (1)	45
C(1)	3157 (2)	1307 (2)	270 (2)	58
C(2)	1859 (2)	141 (2)	1527 (1)	41
C(3)	−293 (3)	−703 (2)	2362 (2)	67
C(4)	−386 (2)	1234 (2)	1378 (1)	43
C(5)	601 (2)	1796 (2)	773 (1)	42
C(6)	101 (2)	2722 (2)	130 (1)	55
C(7)	−1424 (2)	3069 (2)	111 (2)	65
C(8)	2393 (2)	2515 (2)	706 (2)	62
C(9)	−1889 (2)	1582 (2)	1356 (2)	54
C(1')	3202 (2)	−150 (1)	2239 (1)	39
C(2')	3475 (2)	523 (2)	3106 (1)	42
C(3')	4789 (2)	324 (2)	3706 (1)	51
C(4')	5809 (2)	−569 (2)	3469 (2)	59
C(5')	5533 (2)	−1272 (2)	2642 (2)	62
C(6')	4238 (2)	−1056 (2)	2027 (2)	53
H(2)	166 (2)	−56 (2)	104 (1)	51 (5)
H(6)	80 (2)	315 (2)	−30 (1)	65 (6)
H(7)	−182 (2)	369 (2)	−33 (2)	71 (6)
H(8)	−347 (2)	279 (2)	71 (1)	68 (6)
H(9)	−256 (2)	121 (2)	180 (1)	57 (5)
H(11)	289 (2)	65 (2)	−28 (2)	93 (7)
H(12)	419 (3)	109 (2)	59 (2)	90 (7)
H(13)	323 (2)	214 (2)	−2 (2)	79 (7)
H(31)	41 (3)	−111 (2)	283 (2)	91 (8)
H(32)	−117 (3)	−44 (2)	269 (2)	97 (8)
H(33)	−78 (3)	−128 (3)	177 (2)	130 (11)
H(2')	158 (3)	126 (2)	296 (2)	87 (7)
H(3')	493 (2)	83 (2)	428 (2)	75 (6)
H(4')	672 (2)	−71 (2)	393 (1)	64 (5)
H(5')	623 (2)	−188 (2)	246 (1)	79 (7)
H(6')	404 (2)	−155 (2)	143 (2)	64 (6)

* U_{iso} for H atoms.

Experimental. Crystals grown by sublimation (333 K, 200 Pa). Dimensions (mm): 0·42 × 0·40 × 0·30. Laue symmetry determined by indexing 25 randomly distributed reflections ($18 < 2\theta < 26°$) found by the *SEARCH* routine and centered in the counter aperture of an Enraf–Nonius CAD-4 diffractometer. Cell checked by means of oscillation photographs taken along the three axes. Presence of higher symmetry clearly ruled out by Niggli parameters.

Intensity data collected as described elsewhere (Bélanger-Gariépy & Beauchamp, 1980). $2\theta_{max} = 45°$, $0 \le h \le 9$, $0 \le k \le 11$, $-14 \le l \le 14$. Standards (e.s.d.): $\bar{2}\bar{4}3$ (1·0%), $2\bar{4}\bar{3}$ (1·1%), 243 (0·8%), $\bar{4}34$ (0·6%), $\bar{3}2\bar{4}$ (1·8%), $24\bar{5}$ (0·9%). 1811 unique reflections collected. 115 systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) unambiguously identified the space group $P2_1/c$, 1352 observed, 344 unobserved [$I > 3{\cdot}0\sigma(I)$]. Correction for Lorentz effect and polarization.

Structure solved by direct methods and refined on $|F_o|$ by full-matrix least-squares procedures. Non-hydrogen atoms located by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Hydrogens located by standard Fourier techniques. Function $\sum w(|F_o| - |F_c|)^2$ minimized by full-matrix least squares. $w = 1/\sigma^2(F)$. Parameters refined: scale factor, coordinates (all atoms), anisotropic (C,N,O) or isotropic (H) temperature factors. Final $R = 0{\cdot}032$, $wR = 0{\cdot}039$, $S = 1{\cdot}54$, shift/σ (max.) 0·09, (av.) 0·02. Residual electron density (e Å^{-3}) in final ΔF map: max. = 0·14, min = −0·14.

Scattering curves from Cromer & Mann (1968), except for H (Stewart, Davidson & Simpson, 1965). Programs used, besides *MULTAN*, listed elsewhere (Authier-Martin & Beauchamp, 1977). Final coordinates and thermal parameters are listed in Table 1.*

Discussion. The structure of the title compound is shown in Fig. 1, and interatomic distances and bond angles are listed in Table 2. As expected, the five-membered ring assumes an envelope conformation (Smithson, Duckett & Wieser, 1984; Davidson, Murray, Preston & King, 1979; Harlow & Simonsen, 1976). The unit N(1)—C(5)—C(4)—N(3) is planar within 0·005 Å (2·5σ), and C(2) deviates from this plane by 0·465 (2) Å, creating a flap angle of 30·0°. The methyl groups at N(1) and N(3), as well as the hydroxyphenyl group at C(2), are all equatorial. The

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* Lists of structure factors, thermal parameters, distances and angles involving H atoms, and distances to the weighted least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43852 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

nitrogen lone pairs and H(2) are therefore axial, making the lone pairs and the C(2)—H(2) bond antiperiplanar. The aromatic ring of the benzenediamine unit is planar within 0·001 Å (0·5σ) and makes an angle of only 4° with the N(1)—C(5)—C(4)—N(3) plane.

An important part of the structure of (1) is the strong intramolecular hydrogen bond between N(3) and the phenolic hydroxy group (Teitel'baum, Kudryavtseva, Bel'skii & Ivanov, 1980; Hine & Khan, 1977). The N(3)···O(2′) separation [2·709 (2) Å] lies on the low side of the range (2·62–2·93 Å) for this type of hydrogen bond (Stout & Jensen, 1968). To allow this internal bond to be formed and to minimize destabilizing interactions with the methyl groups, the mean plane of the hydroxyphenyl group lies at an angle of 77° with respect to the plane defined by N(1)—C(5)—C(4)—N(3). No appreciable strain is introduced in the ring connecting the hydrogen-bonded atoms, since the angles are all normal and similar to the corresponding angles in 2-methylphenol (Bois, 1972). However, the following atom-to-mean-plane distances (Å) show that the hydroxyphenyl ring departs slightly, but significantly, from planarity: C(1′) 0·013 (2); C(2′) −0·015 (2); C(3′) 0·007 (2); C(4′) 0·011 (2); C(5′) −0·014 (2); C(6′) −0·004 (2). The deviation for O(2′) [0·062 (1) Å] is even greater than for C(2′), and both atoms are displaced from the mean plane in the direction of the hydrogen-bonding partner N(3). Similar but somewhat smaller displacements of oxygen occur in 2-methylphenol (Bois, 1972). These distortions may be particularly advantageous in (1) because internal hydrogen bonding is strengthened while repulsive intramolecular interactions involving C(5′) and C(6′) are simultaneously decreased. Another effect that might be due to hydrogen bonding is a small but significant lengthening of the C(4)—N(3) bond [1·416 (2) Å] relative to C(5)—N(1) [1·399 (2) Å].

Note that the asymmetric structure shown in Fig. 1 is more stable in the solid state than the symmetric alternative (2), which contains a bifurcated hydrogen bond (Olovsson & Jönsson, 1976). Although the structure shown in Fig. 1 is chiral, crystals of (1) are not, since each molecule in the $P2_1/c$ unit cell is related to an enantiomeric counterpart by the center of symmetry.

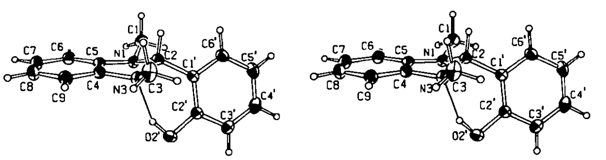
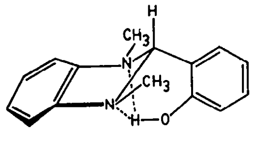


Fig. 1. *ORTEP* (Johnson, 1976) stereoview of (1) showing the atomic numbering. Ellipsoids correspond to 35% probability. Single line represents a hydrogen bond.



(2)

X-ray crystallographic study therefore confirms that (1) contains a C—H bond activated as a donor of hydride by two antiperiplanar lone pairs. We are now studying the redox chemistry of (1) and other dihydrobenzimidazoles designed to bind electrophilic substrates and reduce them by an internal transfer of hydride.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

N(1)–C(2)	1·471 (2)	C(2)–C(1′)	1·507 (2)
N(1)–C(5)	1·399 (2)	C(1′)–C(2′)	1·396 (2)
N(1)–C(1)	1·452 (2)	C(1′)–C(6′)	1·384 (2)
C(2)–N(3)	1·475 (2)	C(2′)–C(3′)	1·384 (2)
N(3)–C(3)	1·459 (3)	C(2′)–O(2′)	1·362 (2)
N(3)–C(4)	1·416 (2)	C(3′)–C(4′)	1·374 (3)
C(4)–C(5)	1·392 (2)	C(4′)–C(5′)	1·368 (3)
C(4)–C(9)	1·380 (2)	C(5′)–C(6′)	1·385 (3)
C(5)–C(6)	1·377 (2)	C(2)–H(2)	1·01 (2)
C(6)–C(7)	1·399 (3)	O(2′)–H(2′)	0·95 (2)
C(7)–C(8)	1·369 (3)	H(2′)–N(3)	1·83 (2)
C(8)–C(9)	1·390 (3)	O(2′)–N(3)	2·709 (2)
C(2)–N(1)–C(5)	106·3 (1)	C(2)–C(1′)–C(2′)	121·1 (1)
C(2)–N(1)–C(1)	116·8 (1)	C(2)–C(1′)–C(6′)	120·6 (1)
C(5)–N(1)–C(1)	120·6 (1)	C(2′)–C(1′)–C(6′)	118·2 (1)
N(1)–C(2)–N(3)	101·6 (1)	C(1′)–C(2′)–C(3′)	120·3 (2)
N(1)–C(2)–C(1′)	112·2 (1)	C(1′)–C(2′)–O(2′)	121·5 (1)
N(3)–C(2)–C(1′)	113·3 (1)	C(3′)–C(2′)–O(2′)	118·2 (1)
C(2)–N(3)–C(4)	105·5 (1)	C(2′)–C(3′)–C(4′)	120·2 (2)
C(2)–N(3)–C(3)	115·1 (1)	C(3′)–C(4′)–C(5′)	120·4 (2)
C(4)–N(3)–C(3)	119·0 (1)	C(4′)–C(5′)–C(6′)	119·7 (2)
N(3)–C(4)–C(5)	108·2 (1)	C(5′)–C(6′)–C(1′)	121·2 (2)
N(3)–C(4)–C(9)	130·2 (2)	C(2′)–O(2′)–H(2′)	104·8 (14)
C(5)–C(4)–C(9)	121·5 (2)	O(2′)–H(2′)–N(3)	152·3 (20)
C(4)–C(5)–N(1)	108·7 (1)	N(1)–C(2)–H(2)	109·3 (9)
C(4)–C(5) C(6)	120·7 (2)	N(3)–C(2)–H(2)	109·0 (9)
C(6)–C(5)–N(1)	130·5 (2)	C(1′)–C(2)–H(2)	111·0 (9)
C(5)–C(6)–C(7)	117·5 (2)		
C(6)–C(7)–C(8)	121·7 (2)		
C(7)–C(8)–C(9)	120·8 (2)		
C(8)–C(9)–C(4)	117·8 (2)		

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Structure of 2,4-Dioxo-1,2,3,4,6,7,8,9-octahydro-10H^+-pyrimido[4,5-*b*]quinolinium Trifluoroacetate Trifluoroacetic Acid Solvate

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Abstract. $\mathrm{C_{11}H_{12}N_3O_2^+.C_2F_3O_2^-.C_2HF_3O_2}$, $M_r = 445·28$, monoclinic, $C2/c$, $a = 24·063\ (8)$, $b = 8·236\ (2)$, $c = 18·523\ (3)$ Å, $\beta = 100·39\ (2)°$, $V = 3610·8\ (1)$ Å^3, $Z = 8$, $D_x = 1·638$, $D_m = 1·620$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·5418$ Å, $\mu = 15·047$ cm^{-1}, $F(000) = 1808$, $T = 296$ K, $R = 0·065$ for 2279 observed reflections. The molecule is a 2,4-disubstituted tricyclic linear system and is protonated. Associated with each cation are two trifluroacetic acid molecules, only one of which is ionized.

Introduction. As part of a research effort directed towards the synthesis of tricyclic folate antimetabolites as potential antitumor agents, we were interested in the synthesis of the linear compound 2,4-dioxo-1,2,3,4,-6,7,8,9-octahydropyrimido[4,5-*b*]quinoline. Facile syntheses of such tricyclic systems are carried out by the cyclocondensation of appropriately substituted 6-aminopyrimidines with bis electrophiles. The linear and/or angular structure of the product is predicated on the direction of ring closure (Irwin & Wibberley, 1969). Each time a new bis electrophile is utilized, the structure of the product needs to be unequivocally proved, usually by an independent synthesis. In two cases where independent synthetic proof of structure was not carried out, a reinvestigation has shown erroneous initial structure assignments (Paterson & Wood, 1972; Wood, Wrigglesworth, Yeowell, Gurney & Hurlbert, 1974; Stark & Breitmaier, 1973; Taylor & Fletcher, 1984). Our new synthesis of tricyclic analogues related to folates (Gangjee, Ohemeng, Tulachka, Lin & Katoh, 1985) required proof of the linear nature of the product and thus its crystal structure determination was undertaken.

Experimental. Crystals were grown by slow evaporation from a trifluroacetic acid–water solution; density measured by flotation in methylene chloride/methylene iodide mixture; clear rectangular needle-like crystal 0·55 × 0·58 × 0·78 mm cleaved from large needle and mounted in glass capillary; Picker FACS-I diffractometer, graphite monochromator; 12 high-angle reflections used for orientation matrix and unit-cell measurements, *hkl* with $h+k \neq 2n$, $h0l$ $l \neq 2n$ absent, space group $C2/c$ chosen based on density, non-chiral nature of molecule and E statistics; absorption corrections based on Howell's analytical expression for polyhedra, min. = 1·927, max. = 2·342; $2\theta_{\max} = 120°$, *hkl* range 0→26, 0→9, −20→20, three standard reflections monitored every 50 reflections, no decay, 2763 reflections measured in θ–2θ scan mode, 2682 unique, $R_{\mathrm{int}} = 0·061$ for duplicates, 403 unobserved $[I < 3\sigma(I)]$; structure solved with *MULTAN*78; all non-hydrogen atoms found from best E map, but only after 20 largest

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