around the two O atoms, O(1) and O(2), are quite distinct. This is noteworthy because complete disorder of the carboxyl group is usually associated with nearly identical environments at the two O atoms (Leiserowitz, 1976). The hydrogen-bond network is of the catemeric type and is identical to that observed in the 4-chloro derivative (1) (Desiraju, Murty & Kishan, 1990). This catemer is generated by a combination of centres of inversion plus a translation along [010] and may be considered to be the primary structural motif in these crystals. The two O···O distances are 2.57 (8) and 2.61 (9) Å [corresponding distances in acid (1) are 2.59 (1) and 2.66 (1) Å]. It should be emphasized that the existence of both *syn* and *anti* O═C—O—H conformations in the structures of these two halogenated phenylpropiolic acids (1) and (2) is quite exceptional (Leiserowitz, 1976; Desiraju, 1989).

The catemer substructures in these two crystals are nearly identical but they are linked by short halogen···halogen contacts in distinctive ways to yield the secondary structure. In acid (1), inversion-related catemers are connected by short C—Cl···Cl—C interactions (Desiraju & Parthasarathy, 1989) [Cl···Cl 3.50 (1) Å] but, in the present structure, Br···Br contacts are found between 2_1-related molecules [Br···Br 3.93 (1) Å; Fig. 2]. In effect, catemers define molecular ribbons and adjacent ribbons are screw or glide related. These alternative secondary motifs may be considered to be triclinic and monoclinic variations of the same structural theme. The monoclinic variation found in this case may be preferred for overall close-packing reasons in that the tilt of the molecular ribbons promotes the formation of aromatic ring herringbone C···H interactions. In turn, tertiary structures are formed in both cases by stacking the secondary structure in the short-axis direction. Such stacking leads to solid-state thermal reactions of the Diels–Alder type for acid (2). Such reactivity has been previously reported (Desiraju & Kishan, 1989). To investigate these issues further, (4-iodophenyl)propiolic acid has been synthesized (m.p. 471 K) but crystals suitable for an X-ray diffraction study have not yet been obtained.

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Structure of Benfotiamine Hemihydrate

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Abstract. Benzenecarbothioic acid *S*-(2-{[(4-amino-2-methyl-5-pyrimidinyl)methyl]formylamino}-1-[2-(phosphonooxy)ethyl]-1-propenyl) ester hemihydrate, $C_{19}H_{23}N_4O_6PS.0.5H_2O$, $M_r = 475.5$, monoclinic, $P2_1/n$, $a = 16.822\ (5)$, $b = 18.556\ (6)$, $c = 14.429\ (5)$ Å, $\beta = 105.52\ (3)°$, $V = 4340\ (1)$ Å^3, $Z = 8$, $D_x = 1.359$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 24.1$ cm^{-1}, $F(000) = 1992$, $T = 295$ K, $R = 0.050$ for 4526 reflections with $I \geq 2\sigma(I)$. The two independent benfotiamine molecules, in the zwitterionic form, assume a similar conformation apart from the phosphonooxyethyl side chains, and maintain structural characteristics of the ring-opened derivatives of thiamin with the *N*-formyl and ethylenic groups nearly perpendicular to each other and the N(3)—C(4) bond retaining single-bond character. The conformation of benfotiamine is stabilized by an intramolecular N(4′α)—H···O(2α) hydrogen bond

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[between the pyrimidine and formyl moieties; 2.978 (5) and 2.952 (6) Å] in both molecules. Crystal packing consists of an extensive hydrogen-bonding network. The two independent molecules assume a similar hydrogen-bonding arrangement and are dimerized *via* the N(4′α)—H···N(3′) hydrogen bonds between the pyrimidine bases. For both independent molecules, a pair of molecules related by a center of symmetry are also dimerized *via* the O—H···O hydrogen bonds between the phosphate groups. The water molecule is disordered statistically in two positions.

Introduction. It is well known that thiamin (vitamin B_1) is labile in the presence of acid, alkali and heat (Dwidevi & Arnold, 1973). The thiazolium ring in thiamin is easily hydrolyzed in mildly alkaline solution to give various thiol or disulfide derivatives which, in turn, can be easily converted to thiamin upon acidification (Hopmann, 1982). Thus far, the crystal structures of five disulfide or thiol derivatives of thiamin have been reported. These include thiamin propyl disulfide (TPD; Nishikawa, Kamiya, Asahi & Matsumura, 1969), thiamin tetrahydrofurfuryl disulfide (TTFD; Shin & Kim, 1986), thiamin disulfide dinitrate (TDD; Shin & Chun, 1987), *O,S*-dibenzoylthiamin (DBT; Shin, 1988) and *O,S*-diacetylthiamin (DAT; Shin & Choi, 1989). In an effort to investigate the structural characteristics of this class of compounds, X-ray analysis of benfotiamine has been undertaken. Benfotiamine, *S*-benzoylthiamin monophosphate, is a ring-opened derivative of thiamin monophosphate and is used as a potent provitamin in East Asian countries.

Experimental. Colorless tabular crystals obtained from an ethanol solution of benfotiamine (Sigma) by slow evaporation at room temperature; crystal *ca* 0.2 × 0.2 × 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 $(1.6 + 0.3\tan\theta)°$, 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 $20 \leq 2\theta \leq 45°$; intensity checks for three standard reflections showed little (± 1%) variation; 6437 independent reflections (h −18 to 18, k 0 to 20, l 0 to 16), 4526 (70%) observed with $I \geq 2\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) and refined by full-matrix least-squares on F with anisotropic thermal parameters using *GX* (Mallinson & Muir, 1985); H atoms identified on a difference map and refined isotropically; H atoms of the disordered water molecule could not be located. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = 1/\{1 + [(F_o - F_B)/F_A]^2\}^2$ where F_A and F_B are empirically adjusted to 200.0 and 30.0; $R = 0.050$ and $wR = 0.055$ for 701 variables, $R = 0.098$ and $wR = 0.094$ for all data; $S = 2.219$; $(\Delta/\sigma)_{\max} = 0.234$ [U_{33} of O(W2)] in final refinement cycle; max. and min. heights in final difference map 0.48 and −0.38 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are given in Table 1.* An *ORTEP* (Johnson, 1976) view of the asymmetric unit with the numbering scheme is shown in Fig. 1. Selected bond distances, bond angles and torsion angles are listed in Table 2. Benfotiamine exists as a zwitterion in which the pyrimidine ring is protonated on N(1′), as in protonated thiamin, and a formal negative charge is delocalized on two O atoms of the phosphate group. The molecular dimensions of the two independent molecules are in agreement within 3σ.

Molecules *A* and *B* are dimerized *via* a pair of N(4′α)—H···N(3′) hydrogen bonds, as frequently observed in the crystal structures of thiamin and its derivatives (Shin & Lah, 1987). The two pyrimidine bases are tilted, with a dihedral angle of 21.0°, in contrast to other cases where the base pair is quite planar. The two molecules are related approximately by a pseudo center of symmetry at (0.50, 0.22, −0.05) except for the portion comprising the 5α-phosphonooxyethyl groups, although the detailed geometries are slightly different as can be seen in the comparison of the dihedral angles listed in Table 2. The conformation of benfotiamine is stabilized in both molecules by an intramolecular N(4′α)—H···O(2α) hydrogen bond [2.978 (5) and 2.952 (6) Å]. This intramolecular hydrogen bond has been observed in all of the ring-opened derivatives except DBT in which N(4′α) is too far from O(2α) [3.539 (5) Å] for hydrogen-bonding interaction to take place, although a favorable N—H···O geometry is still maintained. The overall conformation of benfotiamine is very similar to that of DBT. The *S*-benzoyl group and the pyrimidine ring are *syn* and the 5α side chain and the ring are *anti* with respect to the ethylenic plane. TPD and TTFD have the same relative orientation for the corresponding substituents at S(1) and C(5α) but DAT and TDD have the reversed orientation.

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* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms and molecular dimensions involving the phenyl groups and H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55552 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1007]

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic 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′)	3629 (2)	1473 (2)	1877 (3)	0.035
C(2′)	4350 (3)	1605 (3)	1707 (3)	0.037
N(3′)	4461 (2)	1717 (2)	854 (3)	0.036
C(4′)	3771 (3)	1703 (2)	78 (3)	0.029
C(5′)	2983 (2)	1570 (2)	216 (3)	0.031
C(6′)	2931 (3)	1459 (2)	1117 (3)	0.035
C(2′α)	5094 (3)	1617 (4)	2571 (4)	0.048
N(4′α)	3907 (2)	1818 (2)	−762 (3)	0.038
C(35′)	2219 (3)	1560 (3)	−628 (4)	0.036
N(3)	2022 (2)	2287 (2)	−1061 (3)	0.032
C(2)	2116 (3)	2416 (3)	−1946 (3)	0.039
O(2α)	2419 (2)	2006 (2)	−2412 (2)	0.049
C(4)	1795 (3)	2841 (3)	−494 (3)	0.035
C(4α)	1090 (3)	2646 (3)	−93 (4)	0.051
C(5)	2212 (3)	3461 (3)	−336 (3)	0.036
C(5α)	2001 (3)	4073 (3)	256 (3)	0.043
C(5β)	1620 (3)	4711 (3)	−342 (3)	0.042
O(5γ)	1736 (2)	5358 (2)	247 (2)	0.041
P(5δ)	1020 (1)	5630 (1)	692 (1)	0.032
O(5δ1)	1417 (2)	6223 (2)	1365 (2)	0.040
O(5δ2)	714 (2)	5000 (2)	1166 (2)	0.046
O(5δ3)	321 (2)	5920 (2)	−148 (2)	0.045
S(1)	3052 (1)	3650 (1)	−823 (1)	0.040
C(6)	3901 (3)	3632 (3)	247 (4)	0.044
O(6α)	3807 (2)	3415 (2)	1001 (3)	0.063
C(7)	4691 (3)	3872 (3)	95 (4)	0.045
C(8)	5405 (3)	3748 (3)	835 (4)	0.057
C(9)	6158 (4)	3972 (3)	721 (6)	0.070
C(10)	6214 (4)	4308 (3)	−102 (6)	0.070
C(11)	5508 (4)	4435 (3)	−841 (5)	0.060
C(12)	4752 (3)	4227 (3)	−732 (4)	0.048
Molecule *B*				
N(1′)	6161 (2)	3052 (2)	−1917 (3)	0.034
C(2′)	5474 (3)	2808 (2)	−1746 (3)	0.033
N(3′)	5459 (2)	2457 (2)	−962 (3)	0.032
C(4′)	6189 (3)	2345 (2)	−284 (3)	0.032
C(5′)	6945 (2)	2585 (2)	−427 (3)	0.030
C(6′)	6899 (3)	2947 (2)	−1255 (3)	0.033
C(2′α)	4680 (3)	2924 (3)	−2514 (4)	0.049
N(4′α)	6140 (3)	2002 (2)	504 (3)	0.041
C(35′)	7759 (3)	2436 (3)	289 (4)	0.039
N(3)	8002 (2)	1676 (2)	199 (3)	0.035
C(2)	7963 (3)	1183 (3)	864 (3)	0.040
O(2α)	7693 (2)	1298 (2)	1556 (2)	0.051
C(4)	8179 (3)	1485 (3)	−696 (3)	0.040
C(4α)	8940 (3)	1836 (4)	−840 (5)	0.063
C(5)	7689 (3)	1037 (3)	−1320 (3)	0.040
C(5α)	7807 (4)	843 (3)	−2286 (4)	0.057
C(5β)	8101 (3)	81 (3)	−2347 (4)	0.055
O(5γ)	8970 (2)	37 (2)	−1857 (2)	0.046
P(5δ)	9283 (1)	−595 (1)	−1096 (1)	0.032
O(5δ1)	8877 (2)	−1288 (2)	−1496 (2)	0.041
O(5δ2)	10207 (2)	−567 (2)	−896 (2)	0.042
O(5δ3)	8984 (2)	−406 (2)	−206 (2)	0.045
S(1)	6842 (1)	603 (1)	−1034 (1)	0.047
C(6)	5982 (3)	972 (3)	−1944 (3)	0.044
O(6α)	6081 (2)	1446 (2)	−2467 (2)	0.050
C(7)	5167 (3)	670 (3)	−1929 (4)	0.048
C(8)	4475 (3)	930 (3)	−2627 (4)	0.053
C(9)	3697 (4)	691 (4)	−2650 (5)	0.064
C(10)	3588 (4)	181 (4)	−2009 (5)	0.072
C(11)	4260 (4)	−85 (4)	−1314 (5)	0.075
C(12)	5051 (4)	153 (3)	−1280 (4)	0.064
O(*W*1)	368 (9)	1080 (10)	8067 (10)	0.190
O(*W*2)	1132 (14)	138 (12)	7794 (13)	0.231

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

	Molecule *A*	Molecule *B*
N(1′)—C(2′)	1.323 (6)	1.324 (6)
N(1′)—C(6′)	1.376 (6)	1.363 (6)
C(2′)—N(3′)	1.310 (6)	1.311 (6)
C(2′)—C(2′α)	1.512 (7)	1.505 (7)
N(3′)—C(4′)	1.381 (6)	1.366 (6)
C(4′)—C(5′)	1.414 (6)	1.414 (6)
C(4′)—N(4′α)	1.310 (6)	1.325 (6)
C(5′)—C(6′)	1.342 (6)	1.355 (6)
C(5′)—C(35′)	1.516 (6)	1.504 (6)
C(35′)—N(3)	1.486 (7)	1.484 (7)
N(3)—C(2)	1.349 (6)	1.340 (6)
N(3)—C(4)	1.428 (6)	1.445 (6)
C(2)—O(2α)	1.214 (6)	1.221 (5)
C(4)—C(4α)	1.496 (7)	1.500 (7)
C(4)—C(5)	1.335 (8)	1.336 (7)
C(5)—C(5α)	1.519 (7)	1.503 (7)
C(5)—S(1)	1.773 (5)	1.779 (5)
C(5α)—C(5β)	1.504 (7)	1.508 (8)
C(5β)—O(5γ)	1.454 (6)	1.446 (6)
O(5γ)—P(5δ)	1.591 (4)	1.596 (4)
P(5δ)—O(5δ1)	1.501 (4)	1.497 (4)
P(5δ)—O(5δ2)	1.513 (4)	1.504 (4)
P(5δ)—O(5δ3)	1.542 (3)	1.540 (3)
S(1)—C(6)	1.801 (5)	1.808 (5)
C(6)—O(6α)	1.209 (7)	1.199 (6)
C(6)—C(7)	1.473 (7)	1.487 (7)
N(3′)—C(2′)—N(1′)	124.9 (4)	123.4 (4)
C(4′)—N(3′)—C(2′)	117.3 (4)	118.2 (4)
C(5′)—C(4′)—N(3′)	120.4 (4)	121.3 (4)
C(5′)—C(6′)—N(1′)	120.4 (4)	121.0 (4)
C(6′)—N(1′)—C(2′)	119.0 (4)	119.8 (4)
C(6′)—C(5′)—C(4′)	118.0 (4)	116.3 (4)
C(2′α)—C(2′)—N(1′)	116.6 (4)	117.4 (4)
C(2′α)—C(2′)—N(3′)	118.5 (4)	119.2 (4)
N(4′α)—C(4′)—N(3′)	115.5 (4)	115.9 (4)
N(4′α)—C(4′)—C(5′)	124.1 (4)	122.8 (4)
C(35′)—C(5′)—C(4′)	120.9 (4)	122.1 (4)
C(35′)—C(5′)—C(6′)	121.0 (4)	121.6 (4)
N(3)—C(35′)—C(5′)	111.9 (4)	109.6 (4)
C(2)—N(3)—C(35′)	119.3 (4)	121.2 (4)
O(2α)—C(2)—N(3)	125.9 (5)	124.5 (5)
C(4)—N(3)—C(35′)	118.5 (4)	116.0 (4)
C(4)—N(3)—C(2)	122.1 (4)	122.3 (4)
C(4α)—C(4)—N(3)	114.1 (4)	113.9 (4)
C(5)—C(4)—N(3)	120.6 (4)	121.2 (4)
C(5)—C(4)—C(4α)	125.2 (5)	124.9 (5)
C(5α)—C(5)—C(4)	123.3 (4)	124.3 (5)
C(5β)—C(5α)—C(5)	113.2 (4)	113.9 (5)
O(5γ)—C(5β)—C(5α)	110.2 (3)	109.2 (4)
P(5δ)—O(5δ)—C(5β)	120.0 (3)	118.8 (3)
O(5δ1)—P(5δ)—O(5γ)	103.9 (2)	109.5 (2)
O(5δ2)—P(5δ)—O(5γ)	108.9 (2)	103.9 (2)
O(5δ3)—P(5δ)—O(5γ)	107.1 (2)	106.6 (2)
O(5δ2)—P(5δ)—O(5δ1)	114.9 (2)	116.4 (2)
O(5δ3)—P(5δ)—O(5δ1)	111.5 (2)	107.5 (2)
O(5δ3)—P(5δ)—O(5δ2)	110.2 (2)	112.6 (2)
S(1)—C(5)—C(4)	122.7 (4)	120.9 (4)
S(1)—C(5)—C(5α)	114.0 (4)	114.8 (4)
C(6)—S(1)—C(5)	100.9 (2)	101.2 (2)
O(6α)—C(6)—S(1)	120.9 (4)	121.1 (4)
C(7)—C(6)—S(1)	114.0 (4)	114.1 (4)
C(7)—C(6)—O(6α)	125.1 (5)	124.7 (4)
C(8)—C(7)—C(6)	117.5 (5)	116.8 (5)
C(12)—C(7)—C(6)	123.2 (5)	124.5 (5)
C(4′)—C(5′)—C(35′)—N(3)	−68.1 (5)	76.6 (5)
C(5′)—C(35′)—N(3)—C(2)	110.8 (5)	−106.8 (5)
C(35′)—N(3)—C(4)—C(5)	123.7 (6)	−112.1 (6)
C(2)—N(3)—C(4)—C(5)	−51.7 (5)	60.3 (5)
C(4)—C(5)—C(5α)—C(5β)	−108.2 (6)	108.7 (7)
C(4)—C(5)—S(1)—C(6)	−110.4 (5)	117.1 (5)
C(5)—C(5α)—C(5β)—O(5γ)	−157.2 (5)	−76.2 (5)
C(5α)—C(5β)—O(5γ)—P(5δ)	−96.9 (4)	131.0 (5)
C(5)—S(1)—C(6)—C(7)	−172.0 (4)	176.5 (4)
S(1)—C(6)—C(7)—C(8)	−168.2 (6)	−179.3 (6)

A stereoscopic packing diagram is shown in Fig. 2. Crystal packing consists of an extensive hydrogen-bonding network. The geometrical details of the hydrogen bonds and close contacts are listed in Table 3. The two independent molecules assume a similar hydrogen-bonding arrangement. For both molecules *A* and *B*, a pair of molecules related by a center of symmetry are dimerized *via* the O(5δ3)—H···O(5δ2) hydrogen bonds. Two O(5δ1) atoms are involved in strong hydrogen bonds with N(1′) and at the same time are in short contacts with C(6′) in both molecules which may be regarded as weak C—H···O hydrogen bonds. There are also several short intramolecular C—H···O contacts, some of which may be regarded as very weak hydrogen bonds (Taylor & Kennard, 1982). There are two kinds of ring-stacking interaction. The phenyl ring of *A* and the pyrimidine ring of *B* in the molecular dimer are stacked with a mean separation of 3.302 (4) Å. The dihedral angle between the two planes is 2.4° and the extent of the areal overlap is ~53%. The same phenyl ring of *A* is stacked with the phenyl ring of the centrosymmetrically related molecule *A* with a mean separation of 3.326 (6) Å. The extent of the areal overlap is ~24%. The water molecule is disordered statistically in two positions with occupancy factors of 0.55 and 0.45. The closest contacts are 3.07 (2) Å to O(5γ*B*) and 3.05 (2) Å to O(5δ2*B*) for the major and minor sites, respectively.

It has been suggested that the great reactivity of the ring-opened derivatives toward ring-closing reactions is related to their conformational characteristics, namely, the perpendicular arrangement of the ethylenic and *N*-formyl planes practically forbids the interaction between the lone-pair electrons of N(3) and the ethylenic π orbital and thus the N(3)—C(4) bond remains a single bond for easy rotation. In addition to this, non-bonded intramolecular attraction between S(1) and C(2) has been suggested as facilitating ring closure (Shin & Choi, 1989). All of the structural characteristics are maintained in benfotiamine. S(1)···C(2) separations in benfotiamine are 2.997 (5) and 3.074 (5) Å, for molecules *A* and *B*, respectively, which are much shorter than the expected van der Waals contact of 3.50 Å (Bondi, 1964). The C(4)═C(5) ethylenic double bond and the four atoms attached to it are planar with maximum deviations of 0.012 (5) and 0.088 (7) Å for molecules *A* and *B*, respectively. The five atoms around N(3), including the formyl group, are planar with maximum deviations of 0.076 (5) and 0.074 (5) Å. The dihedral angles between these two planar groups are 128.3 and 119.8° for *A* and *B*, respectively. The two N(3) atoms are 0.037 (4) and 0.053 (5) Å from the planes formed by C(2), C(4) and C(35′), indicating a near-sp^2 hybridization of N(3). The bond distances around N(3) indicate that the lone-pair electrons of N(3) are delocalized mainly through the C(2)—N(3) [1.349 (6) and 1.340 (6) Å] bonds by conjugation with the formyl groups, but only slightly through the N(3)—C(35′) [1.486 (7) and 1.484 (7) Å] and N(3)—C(4) [1.428 (6) and 1.445 (6) Å] bonds. The pyrimidine rings are planar with maximum deviations of 0.005 (6) and 0.008 (4) Å, and the phenyl groups are planar with maximum deviations of 0.010 (6) and 0.008 (7) Å for *A* and *B*, respectively.

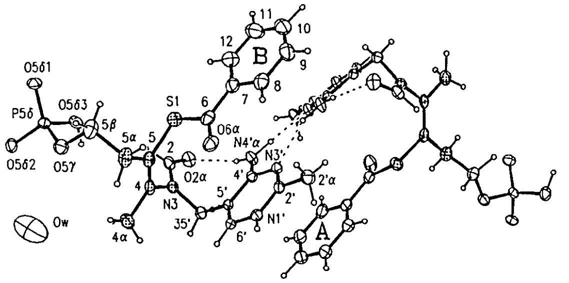

Fig. 1. *ORTEP* (Johnson, 1976) view of the asymmetric unit with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The dotted lines denote hydrogen bonds. Atoms with dots are those in the ethylenic plane.

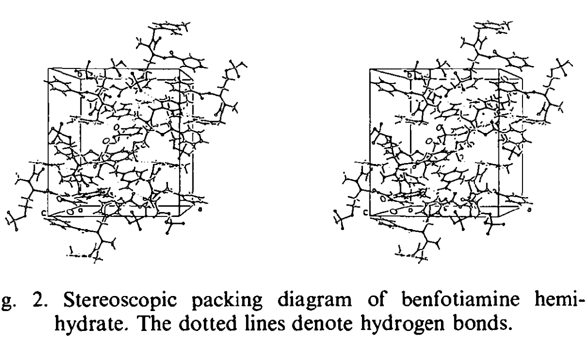

Fig. 2. Stereoscopic packing diagram of benfotiamine hemihydrate. The dotted lines denote hydrogen bonds.

Table 3. *Hydrogen bonds and close contacts* (Å, °)

To simplify the table, full H-atom labels have been omitted, *e.g.* N(4′α*A*)—H(2)···O(2α*A*) means the hydrogen bond from N(4′α) in molecule *A* to O(2α) in molecule *A via* H atom No. 2 on N(4′α). If no label is given there is only one H atom.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(4′α*A*)—H(2)···O(2α*A*)	0.80 (4)	2.19 (4)	2.978 (5)	173 (4)
N(4′α*B*)—H(2)···O(2α*B*)	0.80 (7)	2.18 (7)	2.952 (6)	162 (7)
N(4′α*A*)—H(1)···N(3′*B*)	0.96 (5)	2.04 (5)	2.951 (5)	158 (3)
N(4′α*B*)—H(1)···N(3′*A*)	1.01 (5)	2.04 (5)	3.046 (6)	175 (3)
O(5δ3*A*)—H···O(5δ2*A*^{i})	1.04 (15)	1.56 (15)	2.595 (5)	176 (14)
O(5δ3*B*)—H···O(5δ2*B*^{ii})	1.04 (9)	1.51 (9)	2.546 (5)	172 (8)
N(1′*A*)—H···O(5δ1*A*^{iii})	0.99 (5)	1.61 (6)	2.600 (5)	177 (5)
N(1′*B*)—H···O(5δ1*B*^{iv})	0.93 (5)	1.65 (6)	2.582 (5)	176 (5)
C(6′*A*)—H···O(5δ1*B*^{v})	1.06 (3)	2.20 (3)	3.247 (6)	171 (3)
C(6′*B*)—H···O(5δ1*A*^{vi})	0.92 (5)	2.37 (5)	3.265 (6)	164 (4)
C(35′*A*)—H(1)···O(2α*A*)	0.94 (4)	2.34 (4)	2.809 (6)	111 (3)
C(35′*B*)—H(1)···O(2α*B*)	0.97 (4)	2.39 (4)	2.815 (6)	106 (3)
C(5α*A*)—H(2)···O(6α*A*)	0.95 (6)	2.56 (6)	3.183 (6)	124 (4)
C(5α*B*)—H(2)···O(6α*B*)	0.94 (6)	2.36 (6)	3.057 (7)	131 (5)

Symmetry code: (i) $-x, 1-y, -z$; (ii) $2-x, -y, -z$; (iii) $0.5-x, -0.5+y, 0.5-z$; (iv) $1.5-x, 0.5+y, -0.5-z$; (v) $1-x, -y, -z$; (vi) $1-x, 1-y, -z$.

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2,2,6,6-Tetramethylpiperidine-l-oxyl-4-yl α-D-Glucopyranoside*

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Abstract. $C_{15}H_{28}NO_7$, $M_r = 334.39$, monoclinic, $P2_1$, $a = 9.239$ (4), $b = 14.475$ (6), $c = 6.404$ (3) Å, $\beta = 91.19$ (5)°, $V = 856.25$ Å^3, $Z = 2$, $D_m = 1.297$, $D_x = 1.303$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 0.766$ mm^{-1}, $F(000) = 362.00$, $T = 293$ K, final $R = 0.040$ for 1395 observed reflections. The sugar moiety adopts a $^4C_1$ conformation. The piperidine moiety has a chair conformation in which four ring atoms are planar. The glycosidic linkage is confirmed to be α. Strong intermolecular three-dimensional hydrogen bonding exists in the crystal structure.

Introduction. The spin-labelled sugar 2,2,6,6-tetramethylpiperidine-1-oxyl-4-yl α-D-glucopyranoside (TEMPOG) has been synthesized as described by Stassinopoulou & Troganis (1990). The saccharide has been used as a probe to study the modes of interaction of the legume lectin concanavalin A (con A) with carbohydrate ligands (Stassinopoulou & Troganis, 1990). We have been performing modelling studies of con A–saccharide complexes combining evidence from ^{1}H NMR, ESR and fluorescence measurements, semi-empirical energy calculations and interactive graphics modelling, which require precise molecular geometries (Hamodrakas, Alexandraki, Troganis & Stassinopoulou, 1989). In this report, we present the molecular geometry of TEMPOG, currently used in similar modelling studies (Hamodrakas, Alexandraki, Troganis & Stassinopoulou, 1992), as determined by X-ray crystallography.

Experimental. Crystals were grown from methanol as pale-orange prisms. Unit-cell parameters and space group were determined from precession photographs and refined by least-squares refinement of the setting angles for 12 high-angle ($40 < 2\theta < 60°$) reflections automatically centered on a Picker Facs-1 diffractometer. D_m by flotation. Intensity data were collected at room temperature from a crystal of dimensions 0.4 × 0.6 × 0.4 mm using Ni-filtered Cu $K\alpha$ radiation and θ–2θ scan mode. A total of 1529 unique reflections (after merging equivalents, merging $R_{\rm int} = 0.05$) were recorded, of which 1395 were considered observed at the 3σ level [$I > 3\sigma(I)$]. 2θ range was $3 < 2\theta < 130°$. Index range: -10 to 10 (h), 0 to 17 (k), 0 to 7 (l). Intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved in $P2_1$ by direct

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* 4-(α-D-Glucopyranosyloxy)-2,2,6,6-tetramethylpiperidine 1-oxide.

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