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Structure of 1,3-Dihydro-4-[(2*R*)-2,5-dihydro-2-furyl]-3-phenyl-1-(*p*-tolyl)-2*H*-imidazole-2-thione, $C_{20}H_{18}N_2OS$

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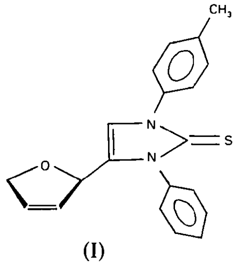
Abstract. $M_r = 334{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}366\,(4)$, $b = 20{\cdot}616\,(5)$, $c = 9{\cdot}137\,(4)$ Å, $V = 1764\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}18$ mm^{-1}, $F(000) = 704$, $T = 300$ K, final $R = 0{\cdot}056$ ($wR = 0{\cdot}052$) for 1979 observed reflections [$I > 2\sigma(I)$]. The furanose ring is approximately planar because of the double bond, 1·289 (9) Å, which affects the conformation of the ring. The dihedral angle between the furanose and imidazole least-squares planes is 69·9 (2)°. A possible C—H···O hydrogen bond has been detected involving C and O atoms in the furanose ring, giving infinite helical chains along [001].

Introduction. The title compound (I) has been obtained by the reaction of 1,3-dihydro-4-(2,3-di-*O*-tosyl-*β*-D-erythrofuranosyl)-3-phenyl-1-(*p*-tolyl)-2*H*-imidazole-2-thione with sodium iodide and zinc powder in dimethylformamide. A study with the ^{1}H NMR technique in solution showed an approximate planar conformation for the furyl ring (Fernández-Bolaños Guzmán, 1984), in agreement with the solid-state results from X-ray data.



(I)

The number of dihydrofuryl heterocycles studied is very small, and this is one of the first (dihydrofuryl)dihydroimidazole-2-thione compounds studied (see also Moreno, López-Castro & Márquez, 1985). Both compounds form part of a wide research project involving the synthesis and structural analysis of imidazole *C*-nucleosides (Criado, Conde & Márquez, 1983; Conde, López-Castro & Márquez, 1978).

Experimental. Dark-yellow parallelepiped crystals supplied by Professor Fernández-Bolaños of the Organic Chemistry Department of this University. Preliminary studies consistent with orthorhombic symmetry; space group $P2_12_12_1$ from systematic absences. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated radiation. Crystal 0·15 × 0·39 × 0·80 mm. Unit-cell parameters from least-squares fit of 25 reflections, $7 < \theta < 16°$. 2877 reflections with $\theta < 30°$ ($0 \leq h \leq 13$, $0 \leq k \leq 28$, $0 \leq l \leq 12$) measured. ω–2θ scan mode. 1979 reflections with $I > 2\sigma(I)$ observed. Intensity changes in two reference reflections less than 2%. Lorentz and polarization corrections. No absorption or extinction effects considered. Weighted tangent-formula refinement (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) of 246 reflections with $E > 1{\cdot}5$. Full-matrix least-squares refinement of 217 parameters based on F_o with observed reflections (*CRYLSQ* of *XRAY*70; Stewart, Kundell & Baldwin, 1970). A Fourier difference synthesis gave the H-atom positions; least-squares refinement in a mixed mode with isotropic temperature factors for H atoms those of the attached non-H atoms gave $wR = 0{\cdot}052$ ($R = 0{\cdot}056$). Weighting scheme $1/\sigma^2(I)$ from counting statistics. Final-cycle parameter shifts less than $0{\cdot}15\sigma$, average $0{\cdot}07\sigma$. $S = 1{\cdot}89$ for 271 variables. Final difference Fourier excursions $-0{\cdot}25 < \Delta\rho < 0{\cdot}30$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Absolute configuration from chemical information.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1956) for non-H atoms are given in Table 1.* Bond angles and distances for non-H atoms are shown in Table 2. The C—H bond distances range from 0·85 (6) to 1·09 (6) Å, with a mean value of 0·95 (6) Å.

Phenyl groups. The value of the C—C bond length is 1·384 (8) Å in the N(1)-phenyl ring and 1·383 (8) Å in the N(2)-phenyl ring. The average C—C—C bond angle is 120·0 (5)° in both rings. The slight deviation from

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42176 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* (×10⁴) *and equivalent isotropic thermal parameters* (×10³) *for the non-*H *atoms, with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2)
S	6374 (1)	1653 (1)	7572 (1)	51 (1)
O	6996 (4)	4369 (2)	6564 (5)	76 (2)
N(1)	7743 (5)	2330 (2)	5412 (4)	48 (1)
N(2)	7358 (4)	2903 (2)	7362 (4)	42 (1)
C(1)	7151 (5)	2293 (2)	6790 (5)	39 (1)
C(2)	8254 (6)	2948 (2)	5147 (5)	52 (2)
C(3)	8012 (5)	3310 (2)	6347 (5)	44 (1)
C(4)	8311 (6)	4016 (2)	6604 (6)	51 (2)
C(5)	7013 (8)	4795 (3)	5298 (9)	89 (3)
C(6)	8504 (8)	4746 (3)	4732 (7)	75 (2)
C(7)	9218 (6)	4311 (3)	5432 (7)	60 (2)
C(8)	6887 (5)	3100 (2)	8802 (5)	39 (1)
C(9)	7908 (6)	3237 (3)	9859 (5)	52 (2)
C(10)	7452 (7)	3472 (3)	11224 (6)	65 (2)
C(11)	6018 (8)	3539 (3)	11497 (6)	68 (2)
C(12)	5026 (6)	3380 (3)	10459 (7)	66 (2)
C(13)	5459 (5)	3163 (3)	9080 (6)	55 (2)
C(14)	7679 (5)	1831 (2)	4316 (5)	43 (1)
C(15)	8419 (6)	1266 (3)	4472 (5)	58 (2)
C(16)	8350 (7)	796 (6)	3388 (6)	63 (2)
C(17)	7508 (6)	890 (2)	2146 (6)	54 (2)
C(18)	6785 (6)	1471 (3)	1994 (6)	57 (2)
C(19)	6864 (5)	1945 (2)	3065 (6)	50 (2)
C(20)	7438 (8)	377 (3)	978 (7)	86 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S—C(1)	1·677 (5)	C(8)—C(9)	1·389 (7)
O—C(4)	1·431 (6)	C(8)—C(13)	1·368 (7)
O—C(5)	1·452 (9)	C(9)—C(10)	1·404 (8)
N(1)—C(1)	1·378 (6)	C(10)—C(11)	1·373 (9)
N(1)—C(2)	1·383 (6)	C(11)—C(12)	1·368 (9)
N(1)—C(14)	1·435 (6)	C(12)—C(13)	1·397 (8)
N(2)—C(1)	1·375 (6)	C(14)—C(15)	1·364 (7)
N(2)—C(3)	1·392 (6)	C(14)—C(19)	1·394 (7)
N(2)—C(8)	1·446 (6)	C(15)—C(16)	1·386 (8)
C(2)—C(3)	1·345 (7)	C(16)—C(17)	1·396 (8)
C(3)—C(4)	1·501 (7)	C(17)—C(18)	1·383 (8)
C(4)—C(7)	1·497 (8)	C(17)—C(20)	1·505 (8)
C(5)—C(6)	1·492 (9)	C(18)—C(19)	1·384 (7)
C(6)—C(7)	1·289 (9)		

C(4)—O—C(5)	108·6 (5)	C(4)—C(7)—C(6)	110·1 (5)
C(2)—N(1)—C(14)	123·5 (4)	N(2)—C(8)—C(13)	119·6 (4)
C(1)—N(1)—C(14)	125·6 (4)	N(2)—C(8)—C(9)	118·7 (4)
C(1)—N(1)—C(2)	110·4 (4)	C(9)—C(8)—C(13)	121·6 (5)
C(3)—N(2)—C(8)	124·8 (4)	C(8)—C(9)—C(10)	118·6 (5)
C(1)—N(2)—C(8)	124·0 (4)	C(9)—C(10)—C(11)	119·6 (5)
C(1)—N(2)—C(3)	111·1 (4)	C(10)—C(11)—C(12)	121·0 (6)
N(1)—C(1)—N(2)	103·9 (4)	C(11)—C(12)—C(13)	120·3 (5)
S—C(1)—N(2)	128·5 (4)	C(8)—C(13)—C(12)	118·8 (5)
S—C(1)—N(1)	127·6 (4)	N(1)—C(14)—C(19)	118·3 (4)
N(1)—C(2)—C(3)	108·1 (4)	N(1)—C(14)—C(15)	121·2 (4)
N(2)—C(3)—C(2)	106·4 (4)	C(15)—C(14)—C(19)	120·5 (4)
C(2)—C(3)—C(4)	129·3 (4)	C(14)—C(15)—C(16)	119·9 (5)
N(2)—C(3)—C(4)	124·2 (4)	C(15)—C(16)—C(17)	120·6 (5)
O—C(4)—C(3)	109·2 (4)	C(16)—C(17)—C(20)	120·2 (5)
C(3)—C(4)—C(7)	112·9 (4)	C(16)—C(17)—C(18)	118·6 (5)
O—C(4)—C(7)	105·3 (4)	C(18)—C(17)—C(20)	121·1 (5)
O—C(5)—C(6)	104·2 (6)	C(17)—C(18)—C(19)	120·9 (5)
C(5)—C(6)—C(7)	111·1 (6)	C(14)—C(19)—C(18)	119·4 (5)

theoretical planarity [$\sum(\Delta/\sigma)^2$ 13·27 and 19·75, respectively] could not be real. The dihedral angles between the N(1)- and N(2)-phenyl rings and the imidazole ring are 64·6 (2) and 69·7 (2)° respectively, both within the range 60–80° usually found for the phenyl–imidazole subrotation. The two attached atoms N(1) and N(2) are at 0·004 (4) and 0·082 (4) Å from the respective ring least-squares planes.

Imidazole ring. The observed value of the C—S bond length is 1·677 (5) Å, a little shorter than the 1·694 (3) Å in ethylenethiourea (Battaglia, Bonamartini Corradi & Nardelli, 1984), having partial double-bond character, a characteristic feature in these compounds. Bond lengths and angles are similar to those found in previous compounds (Criado, Conde & Márquez, 1983; Conde, López-Castro & Márquez, 1978). The ring deviates very slightly from theoretical planarity [$\sum(\Delta/\sigma)^2 = 16\cdot83$; χ^2 at 95% is 5·99] and the maximum atomic displacement from the least-squares plane is 0·012 (5) Å. The three attached atoms C(4), C(14) and C(8) are at 0·070 (5), 0·129 (5) and 0·020 (4) Å from the best plane.

Furyl ring. The furyl ring has a special conformation as a consequence of the presence of the C(6)=C(7) bond, which strongly affects the geometry of the ring. The C(6)=C(7) double-bond length is 1·289 (9) Å, quite similar to that found for 1,3-dihydro-4-[(2*S*)-2,5-dihydro-2-furyl]-3-methyl-1-(*p*-tolyl)-2*H*-imidazole-2-thione, 1·297 (7) Å (Moreno, López-Castro & Márquez, 1985), but significantly shorter than the normal C=C bond length of 1·337 (6) Å (*International Tables for X-ray Crystallography*, 1962). Bonds of a similar length have been found previously [1·31 (2) Å (Galloy & Watson, 1983); 1·295 (6) Å (Mazhar-ul-Haque, Ahmed & Horne, 1983)]. The endocyclic bonds O—C(4) 1·431 (6) and O—C(5) 1·452 (9) Å show the typical asymmetry due to anomeric effects. The average C—C single bond is 1·494 (9) Å.

Bond-angle values for the ring are: C(4)—O—C(5) 108·6 (5), O—C—C 104·8 (5) av. and C—C—C 110·6 (6)° av. Bond lengths and angles are in agreement with those found in the above-mentioned compound. The ring is approximately planar and the maximum atomic deviation from the least-squares plane is 0·068 (7) Å [$\sum(\Delta/\sigma)^2 = 202\cdot11$]. In terms of ring-puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $Q = 0\cdot079$ (6) Å and $\varphi = 171$ (5)° for the sequence O—C(4)—C(7)—C(6)—C(5). The dihedral angle between the imidazole and furyl least-squares planes is 69·9 (2)°, differing from the 99·1 (2)° found for the above-mentioned compound. The glycosidic angle O—C(4)—C(3)—C(2) (Sundaralingam, 1969) is 105·6 (6)° and corresponds to the *syn* configuration (Pullman, 1976).

Crystal packing. Fig. 1 shows the contents of the unit cell viewed along **c**. Packing is due to the hydrogen bond C(6)—H(6)···O($\frac{3}{2}-x$, $1-y$, $-\frac{1}{2}+z$). Each

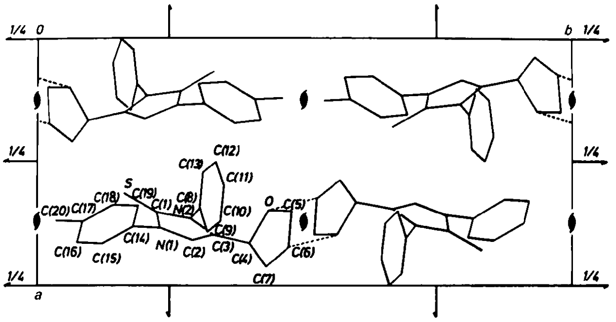

Fig. 1. The unit cell viewed along **c**. Broken lines are hydrogen bonds.

molecule is linked by a hydrogen bond to another molecule related by a twofold screw axis parallel to **c**, giving rise to infinite helical chains parallel to [001]: C(6)—H(6) 0·94 (6), C(6)···O 3·454 (8), H(6)···O 2·66 (6) Å and C(6)—H(6)···O 143 (5)°. No other intermolecular contacts shorter than the sum of the van der Waals radii have been detected. This type of hydrogen bond linking a C—H group with an O atom, both from the sugar ring, is not usual for the imidazole *C*-nucleosides studied. It is known that the ring-O atom is also excluded from the hydrogen-bonding schemes in pyranose crystal structures (Jeffrey & Lewis, 1978).

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Structures of Four Derivatives of 5,7-Dichloro-2,3-dihydro-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine

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Abstract. Compound (II): 5,7-dichloro-2-ethoxy-2,3-dihydro-4-(*p*-nitrobenzoyl)-4*H*-1,4-benzoxazine, $C_{17}H_{14}Cl_2N_2O_5$, $M_r = 397$, triclinic, $P\bar{1}$, $a = 7\cdot174$ (3), $b = 7\cdot859$ (4), $c = 16\cdot965$ (9) Å, $\alpha = 85\cdot50$ (4), $\beta = 79\cdot27$ (4), $\gamma = 71\cdot62$ (3)°, $V = 891\cdot7$ Å^3, $Z = 2$, $D_x = 1\cdot48$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot0$ cm^{-1},

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