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Structure of 1′-(*p*-Bromophenyl)-3′-ethyl-1′,3′,4′,5′-tetrahydro-1,2-dideoxy-D-*glycero*-D-*gulo*-heptofuranoso[1,2-*d*]imidazole-2′-thione,* $C_{16}H_{21}BrN_2O_5S$

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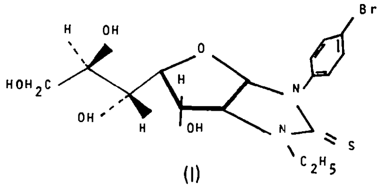
Abstract. $M_r = 433{\cdot}3$, monoclinic, $P2_1$, $a = 6{\cdot}924\,(3)$, $b = 8{\cdot}661\,(1)$, $c = 15{\cdot}039\,(3)$ Å, $\beta = 96{\cdot}92\,(3)°$, $V = 895{\cdot}3\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}598\,(5)$, $D_x = 1{\cdot}607$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 2{\cdot}42$ mm^{-1}, $F(000) = 444$, $T = 300$ K, $R = 0{\cdot}039$ for 2038 observed independent reflexions. The sugar ring adopts a ^4E conformation and the dihedral angle in the bicycle is 49·0 (2)°. Intermolecular hydrogen bonds link the molecules to form a three-dimensional network.

Introduction. The structure determination of the title compound (I) was undertaken as part of a continuing research project in this laboratory involving glucimidazoles and imidazole *C*-nucleosides. Compounds obtained by reaction of 2-deoxy-2-ethyl(propyl)-aminohexose(heptose) with aryl (alkyl) isothiocyanates (García Gonzalez, Galbis-Pérez, Fernandez-Garcia-Hierro & Fernández-Bolaños, 1979; Galbis-Pérez, Pinto Corraliza, Román-Galán & Goméz-Guillén, 1979) have been studied in order to establish the conformational details of the molecule in the solid state. Recently, we have reported the crystal structure of 1′-(*p*-bromophenyl)-3′-ethyl-1′,3′,4′,5′-tetrahydro-1,2-dideoxy-D-*glycero*-L-*gluco*-heptofuranoso[1,2-*d*]imidazole-2′-thione (Estrada, Conde & Márquez, 1983). The title compound has been prepared (Galbis-Pérez, Palacios, Jiménez-Requejo, Avalos & Fernández-Bolaños, 1983) by condensation of 2-amino-2-deoxy-D-*glycero*-D-*gluco*-heptose with aryl isothiocyanate (Galbis-Pérez *et al.*, 1979) and separated by fractioned crystallization. Its chemical nature was established from elemental analysis and spectroscopic data and the X-ray analysis was carried out to define its structure and conformation.



(I)

Experimental. Single crystals in the form of prisms elongated along [001] prepared in the Organic Chemistry Department of the University of Extremadura and kindly supplied by Professor J. Galbis. D_m by flotation method. Crystal 0·06 × 0·08 × 0·13 mm. Unit-cell parameters by least squares from 23 reflexions, $5 < \theta < 20°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $2\theta \leq 60°$ ($|h| \leq 9$, $k \leq 12$, $l \leq 21$), ω–2θ scan mode. Three standard reflexions (200, 020, 023): variation in intensity less than 3% of mean value. 2855 independent reflexions measured, 817 considered unobserved [$I < 2\sigma(I)$]. Lorentz and polarization correction, no correction for absorption ($\mu R \sim 0{\cdot}2$) or extinction. Patterson function and heavy-atom method with the initial set of phases based on Br-atom position. Full-matrix least-squares refinement on F, anisotropic. Difference Fourier synthesis revealed the 21 H-atom positions; isotropic temperature factor for each H set equal to that of the atom bonded to it. Further least-squares refinement including the positional parameters of the H atoms and anomalous-dispersion corrections for Br and S atomic scattering factors (*International Tables for X-ray Crystallography*, 1974)

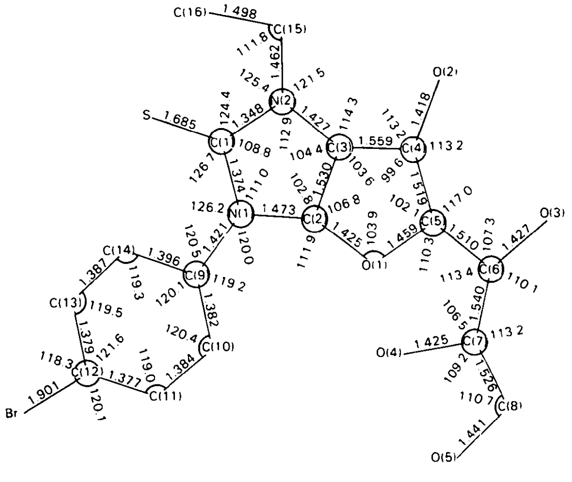


Fig. 1. Bond lengths (Å) and angles (°) in the molecule. (Standard deviations are in the ranges 0·006–0·010 Å and 0·41–0·60°, respectively.)

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* IUPAC name: 6-(*p*-bromophenyl)-4-ethyl-3-hydroxy-2-(1,2,3-trihydroxypropyl)-2,3,3a,5,6,6a-hexahydrofuro[2,3-*d*]imidazole-5(4*H*)-thione.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j \cos(\mathbf{a}_i,\mathbf{a}_j)$ ($\times 10^3$).

	x	y	z	U_{eq}(Å^2)
Br	8953 (1)	0	57 (5)	54 (<1)
S	4655 (2)	−6296 (2)	−2391 (1)	36 (1)
O(1)	263 (5)	−1949 (5)	−2955 (3)	32 (1)
O(2)	−707 (6)	−4450 (5)	−4227 (3)	35 (1)
O(3)	−2427 (6)	272 (6)	−3888 (3)	43 (1)
O(4)	−4409 (7)	−724 (6)	−5485 (3)	44 (2)
O(5)	−7587 (6)	−2267 (6)	−4841 (3)	42 (2)
N(1)	2613 (6)	−3648 (6)	−2162 (3)	27 (1)
N(2)	822 (7)	−5679 (6)	−2619 (4)	32 (2)
C(1)	2658 (7)	−5187 (7)	−2380 (3)	27 (2)
C(2)	599 (7)	−3065 (7)	−2257 (4)	27 (2)
C(3)	−594 (7)	−4494 (7)	−2568 (4)	27 (2)
C(4)	−1683 (7)	−4000 (7)	−3492 (4)	27 (2)
C(5)	−1722 (7)	−2263 (7)	−3357 (4)	28 (2)
C(6)	−2224 (8)	−1280 (8)	−4182 (4)	29 (2)
C(7)	−4093 (8)	−1798 (7)	−4764 (4)	30 (2)
C(8)	−5874 (8)	−1820 (9)	−4257 (4)	7 (2)
C(9)	4114 (7)	−2808 (7)	−1645 (4)	1 (2)
C(10)	4287 (8)	−1242 (8)	−1791 (4)	1 (2)
C(11)	5708 (9)	−389 (7)	−1284 (4)	1 (2)
C(12)	6922 (8)	−1119 (8)	−622 (4)	1 (2)
C(13)	6742 (9)	−2673 (8)	−449 (4)	0 (2)
C(14)	5315 (8)	−3529 (8)	−955 (4)	34 (2)
C(15)	253 (9)	−7267 (8)	−2855 (4)	37 (2)
C(16)	−3 (11)	−8214 (9)	−2044 (5)	49 (2)

reduced R_w to 0·051 ($R = 0{\cdot}049$); weighting scheme based on a statistical count criterion ($w = 1/\sigma^2$). $(\Delta/\sigma)_{\max} = 0{\cdot}3$. $S = 1{\cdot}09$ for 289 refined parameters. Final difference synthesis showed $0{\cdot}35 \geq \Delta\rho \geq -0{\cdot}25$ e Å^{-3}. The enantiomorphic form of the molecule was considered and the final R_w value was 0·041 ($R = 0{\cdot}039$). The application of the $\mathscr{R}$ test (Hamilton, 1965) indicates that the second enantiomorph is correct [$\mathscr{R} = R_w(1)/R_w(2) = 1{\cdot}244$; $\mathscr{R}_{1,1749,\,0{\cdot}005} \simeq 1{\cdot}002$] and, therefore, can be retained as the absolute configuration. Crystallographic programs of the *XRAY70* system (Stewart, Kundell & Baldwin, 1970) used throughout.

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-hydrogen atoms are given in Table 1.* Bond lengths and angles involving non-hydrogen atoms are shown in Fig. 1. C—H bond distances range from 0·83 (9) to 1·15 (9) Å with an average value of 1·03 (9) Å. The average O—H bond length is 0·92 (9) Å.

Molecular geometry

Values of bond lengths and angles in the imidazolidine ring are similar to those reported in other analogous compounds (Conde, Bernier & Márquez, 1980; Estrada, Conde & Márquez, 1983). The typical asymmetry for intracyclic N—C bonds, due to the contribution of the different resonance forms of the thiourea systems (Valle, Cojazzi, Bussetti & Mammi 1970; Estrada, Conde & Márquez, 1983), is observed. The ring is planar as indicated by the $\sum(\Delta/\sigma)^2$ value of 0·94 (χ^2 at 95% 5·59).

Bond lengths and angles in the furanosyl ring are similar to those observed in analogous compounds previously studied and the typical asymmetry of the endocyclic bonds O(1)—C(2) and O(1)—C(5) due to anomeric effects is observed. The glucofuranose ring is not planar as expected. In terms of the ring-puckering coordinates (Cremer & Pople, 1975) the amplitude and phase magnitudes are $Q = 0{\cdot}462\,(5)$ Å and $\varphi = 145{\cdot}2\,(6)°$ for the sequence O(1)—C(2)—C(3)—C(4)—C(5) and the resulting conformation is ^4E. The asymmetry parameter of Duax, Weeks & Rohrer (1976) is ΔC_s [C(5)] = 0·014 (3)°. This puckering mode is different from the twist conformation found in a recently reported analogous compound (Estrada, Conde & Márquez, 1983) but it is similar to those of other analogous compounds (Conde, López-Castro & Márquez, 1978). The small value of the C(4)—C(3)—C(2)—O(1) torsion angle [−2·4 (5)°], characteristic of these compounds, is attributed to distortion of the furanosyl ring due to the ring fusion.

The two rings in the bicycle show a *cis* form of coupling as illustrated in Fig. 2 in which ν_1 and μ_1 are projected valency angles and β, γ and δ torsion angles. The relation $\beta = \gamma$ derived for a *cis* fusion involving only ternary or quaternary C atoms (Geise, Altona & Romers, 1967) holds in this case. As observed in analogous compounds (Conde, López-Castro & Márquez, 1978; Conde, Bernier & Márquez, 1980; Estrada, Conde & Márquez, 1983) the bonds of the C(2) and C(3) carbon atoms are nearly eclipsed. The dihedral angle between the least-squares planes of the imidazolidine and furanosyl rings is 49·3 (3)°. This value is smaller than those found for similar compounds (~ 70°). In the phenyl ring, the atomic deviations from the least-squares plane through the ring atoms are

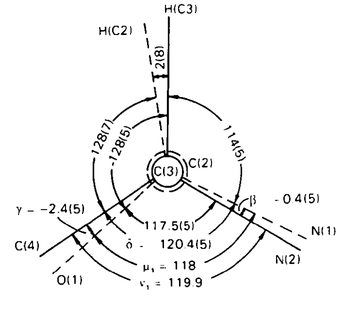

Fig. 2. Newman projection along C(2)—C(3), illustrating the ring fusion (angles in deg).

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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 39192 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

statistically significant: $\sum(\Delta/\sigma)^2 = 19{\cdot}30$ (χ^2 at 95% 7·81); however, this distortion is probably not real.

The phenyl ring is markedly twisted with respect to the imidazolidine plane. The dihedral angle between the least-squares planes through the phenyl and imidazolidine rings is 45·0 (2)°. Values in the range 60–80° for this dihedral angle have been found in similar compounds, except for the value of 15·1 (6)° observed in the case of 1′-phenyl-1′,3′,4′,5′-tetrahydro-1,2-dideoxyglucofuranoso[1,2-*d*]imidazol-2-one (Conde, Bernier & Márquez, 1980) and may indicate a significant contribution of intramolecular interaction. The ethyl group is also twisted with respect to the imidazolidine ring as indicated by the torsion angle C(1)—N(2)—C(15)—C(16) = 85·6 (7)°.

Crystal packing

Fig. 3 shows the contents of the unit cell viewed down the *a* axis. The crystal structure is stabilized by an extensive three-dimensional hydrogen-bonding network. Molecules are linked to form chains parallel to [100] by O(2)—H(O2)···O(5)(x+1, y, z) hydrogen bonds and chains parallel to [010] by C(15)—H(151)···O(3)(x, y−1, z) hydrogen bonds. Also, each molecule is linked to three nearest neighbours related by a twofold screw axis by O(5)—H(O5)···O(2)($-x-1$, $y+\frac{1}{2}$, $-z-1$), O(4)—H(O4)···S($-x$, $y+\frac{1}{2}$, $-z-1$) and C(4)—H(4)···O(4)($-x-1$, $y-\frac{1}{2}$, $-z-1$) hydrogen bonds. Details of these hydrogen bonds are given in Table 2.

Table 2. *Geometry of the hydrogen bonds*

X—H···*Y*	*X*···*Y*(Å)	*X*—H(Å)	H···*Y*(Å)	*X*—H···*Y*(°)
O(2)—H(O2)···O(5^{i})	3·094 (6)	0·86 (9)	2·34 (9)	182 (8)
C(15)—H(15)···O(3^{ii})	3·115 (8)	1·07 (8)	2·43 (9)	120 (6)
O(5)—H(O5)···O(2^{iii})	2·986 (7)	0·96 (9)	2·06 (10)	161 (8)
O(4)—H(O4)···S^{iv}	3·216 (5)	1·03 (9)	2·25 (9)	155 (7)
C(4)—H(4)···O(4^{v})	3·304 (7)	0·97 (8)	2·44 (8)	148 (6)

Symmetry transformations: (i) $x+1$, y, z; (ii) x, $y-1$, z; (iii) $-x-1$, $y+\frac{1}{2}$, $-z-1$; (iv) $-x$, $y+\frac{1}{2}$, $-z-1$; (v) $-x-1$, $y-\frac{1}{2}$, $-z-1$.

For the two O—H···O contacts listed in Table 2 the values of the *d* parameter, defined as the difference between the sum of the van der Waals radii and the interatomic distance (Taylor & Kennard, 1982), are 0·36 and 0·66 Å respectively, both satisfying the rule $d > 0{\cdot}3$ Å, and the O—H···O angles agree with the mean value [165·8 (12)°] for bonds with O···H > 1·812 Å (Allen, Kennard & Taylor, 1983) and so can be described as hydrogen bonds. For the two short C—H···O interactions shown in Table 2 the *d* values are both close to the limiting value $d = 0{\cdot}3$; however, the C(4)—H(4)···O(4) angle is close to the mean value reported for the C—H···O hydrogen bonds (Taylor & Kennard, 1982) but C(15)—H(15)···O(3) is significantly smaller. On the other hand, C(15) is immediately adjacent to an N atom, this fact enhancing the facility to participate in hydrogen bonds (Taylor & Kennard, 1982). The impotance of C—H···O hydrogen bonds in the crystal structures of nucleosides has been recognized (Jeffrey & Maluszynska, 1982). Finally, the existence of short O—H···S contacts has been found in other imidazolidine-2-thione compounds (Vega, Hernández-Montis & López-Castro, 1976; Jiménez-Garay, López-Castro & Márquez, 1976; Criado, Conde & Márquez, 1983) and, perhaps, the negative character associated with the S atom in the resonance forms of the thiourea system is important in the electrostatic-energy term. No other intermolecular contacts significantly shorter than the sums of the van der Waals radii have been detected. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983).

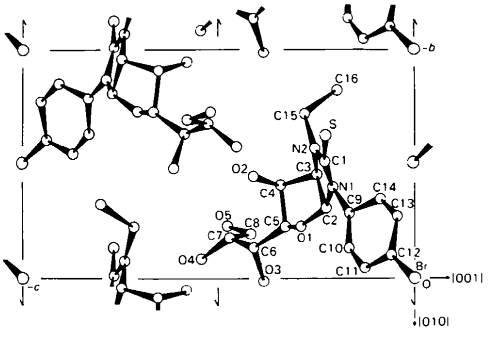

Fig. 3. A view of the cell down **a**.

The authors thank Professor Galbis for supplying the crystals and Dr Gutiérrez-Puebla (University of Madrid) for collecting the data. The present work is part of a research project supported by the Government through the 'Comisión Asesora de Invcstigación Cientifica y Técnica'.

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SHORT COMMUNICATIONS

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Acta Cryst. (1984). C**40**, 901

Structure of 2-amino-3,5-dibromo-*N*-cyclohexyl-*N*-methylbenzenemethanamine–salicylic acid (1:1): corrigendum.*

By RICHARD E. MARSH, *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California* 91125, *USA*

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Abstract

The crystal structure of $C_{14}H_{20}Br_2N_2.C_7H_6O_3$ should be described in the monoclinic space group $C2/c$ rather than the triclinic $P\bar{1}$ reported by Shimizu, Nishigaki, Nakai & Osaki [*Acta Cryst.* (1983), C**39**, 891–893].

The crystal structure of this compound was described as triclinic, space group $P\bar{1}$, with $a = 29{\cdot}146\,(34)$, $b = 9{\cdot}710\,(3)$, $c = 9{\cdot}719\,(9)$ Å, $\alpha = 105{\cdot}18\,(5)$, $\beta = 124{\cdot}18\,(6)$, $\gamma = 85{\cdot}99\,(6)^\circ$, $Z = 4$ (Shimizu, Nishigaki, Nakai & Osaki, 1983). The vectors $[01\bar{1}]$, $[011]$, $[102]$ define a C-centered cell with $a' = 15{\cdot}433$, $b' = 11{\cdot}803$, $c' = 24{\cdot}306$, $\alpha' = 89{\cdot}97$, $\beta' = 99{\cdot}11$, $\gamma' = 90{\cdot}06^\circ$, $Z = 8$.† The corresponding transformations $x' = x + \frac{1}{2}(y - z)$, $y' = -x + \frac{1}{2}(y + z)$, $z' = x$ lead to atomic coordinates that are consistent with the symmetry of the monoclinic space group $C2/c$ within the reported uncertainties. (No translation of origin is necessary since, by even chance, the center of symmetry chosen as origin in the triclinic description corresponds to a conventional origin in $C2/c$.) The $C2/c$ parameters are given in Table 1.

The c-glide plane of $C2/c$ requires the systematic extinction of reflections $hk\bar{k}$ with h odd in the triclinic indexing.

Table 1. *Coordinates* ($\times 10^4$) *for space group* $C2/c$

The $P\bar{1}$ coordinates (Shimizu *et al.*, 1983) have been averaged according to the symmetry of $C2/c$; numbers in square brackets are shifts necessary to achieve this symmetry.

	x'	y'	z'
Br(1)	612 [1]	5140 [0]	4352 [0]
Br(2)	432 [0]	695 [1]	3513 [1]
C(1)	1077 [2]	3766 [12]	2860 [0]
C(2)	996 [8]	4556 [6]	3276 [2]
C(3)	760 [10]	4137 [3]	3768 [2]
C(4)	604 [2]	3002 [2]	3856 [4]
C(5)	673 [6]	2265 [9]	3425 [8]
C(6)	908 [4]	2623 [3]	2935 [4]
N(1)	1164 [1]	5692 [3]	3220 [2]
C(7)	1299 [4]	4099 [2]	2306 [0]
N(2)	2225 [1]	3768 [1]	2252 [0]
C(8)	2878 [4]	4586 [1]	2543 [2]
C(9)	2363 [6]	3544 [4]	1658 [4]
C(10)	2074 [4]	4540 [0]	1276 [2]
C(11)	2233 [2]	4270 [0]	686 [0]
C(12)	1755 [2]	3196 [6]	469 [2]
C(13)	2055 [2]	2215 [2]	856 [6]
C(14)	1917 [2]	2448 [2]	1454 [0]
C(15)	3847 [1]	2707 [5]	3684 [2]
C(16)	4724 [2]	3022 [4]	3882 [2]
C(17)	4938 [10]	3469 [3]	4411 [1]
C(18)	4294 [5]	3621 [5]	4736 [2]
C(19)	3423 [4]	3333 [5]	4549 [0]
C(20)	3207 [2]	2865 [5]	4021 [0]
C(21)	3609 [1]	2233 [3]	3114 [2]
O(1)	2826 [2]	2039 [4]	2930 [2]
O(2)	4222 [0]	2059 [3]	2846 [2]
O(3)	5348 [2]	2897 [1]	3558 [0]

Reference

SHIMIZU, N., NISHIGAKI, S., NAKAI, Y. & OSAKI, K. (1983). *Acta Cryst.* C**39**, 891–893.

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† The relative e.s.d.'s in the triclinic cell translations are highly disparate, and since covariances are not given it is impossible even to estimate appropriate e.s.d.'s for the monoclinic cell dimensions.

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