McConnell, J. F. (1974). *Cryst. Struct. Commun.* **3**, 73–75.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Murray-Rust, P. & Glusker, J. P. (1984). *J. Am. Chem. Soc.* **106**, 1018–1025.

Ravikumar, K., Rajan, S. S., Pattabhi, V. & Gabe, E. J. (1985). *Acta Cryst.* C**41**, 280–282.

Terada, A., Naruto, S., Wachi, K., Tanaka, S., Iizuka, Y. & Misaka, R. (1984). *J. Med. Chem.* **27**, 212–216.

Acta Cryst. (1986). C**42**, 454–457

X-ray Structure and Molecular-Packing Analysis of a Glucofuranosoimidazolidine-2-thione

By M. D. Estrada, A. Conde and R. Márquez

Departamento de Física del Estado Sólido, Facultad de Física, Universidad de Sevilla, Spain

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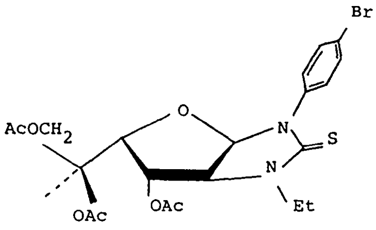
Abstract. 1-(4-Bromophenyl)-3-ethyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-L-glucofuranoso)[2,1-*d*]imidazolidine-2-thione,* $C_{21}H_{25}BrN_2O_7S$, $M_r = 529{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}056\ (7)$, $b = 22{\cdot}420\ (9)$, $c = 8{\cdot}841\ (2)$ Å, $V = 2390\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}47\ (2)$, $D_x = 1{\cdot}47$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}82$ mm^{-1}, $F(000) = 1088$, room temperature, final $R = 0{\cdot}070$ for 1668 observed reflexions. The sugar ring adopts the ^4E conformation and the imidazolidine ring is almost planar. The dihedral angle in the bicyclic system is 71·1 (4)°. The crystal cohesion is mainly due to van der Waals interactions. The lattice energy was computed in the atom–atom approach using van der Waals potential functions and the calculations account satisfactorily for the features of the crystal packing.

Introduction. The structure determination of 1-(*p*-bromophenyl)-3-ethyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-L-glucofuranoso)[2,1-*d*]imidazolidine-2-thione (I) was undertaken as part of a continuing research project on imidazole *C*-glycosides. Recently, some compounds derived from 2-(alkylamino)-2-deoxyheptoses and 2-(alkylamino)-2-deoxyhexoses have been reported (Estrada, Conde & Márquez, 1983, 1984; Conde, Millan, Conde & Márquez, 1985*a*,*b*) and in this paper we report the structure of a tetra-*O*-acetyl derivative. The application of aminonitrile synthesis to the preparation of the new 2-(ethylamino)-2-deoxyhexose having L-*gluco* configuration and its reaction with 4-bromophenyl isothiocyanate to afford the title compound has been recently reported (Galbis Pérez, Palacios Albarrán, Jiménez Requejo & Avalos González, 1984). Its chemical nature was established from elemental analysis and spectroscopic IR and ^{1}H NMR data and the X-ray analysis was suggested in order to establish the conformational details of the molecule in the solid state.



(I)

Experimental. Single crystals in the form of colourless needles elongated along [100] prepared in the Organic Chemistry Department of the University of Extremadura and kindly supplied by Professor J. A. Galbis Pérez. D_m by flotation method. Crystal 0·25 × 0·15 × 0·10 mm. Unit-cell parameters from 25 reflexions, $5 < \theta < 22°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $2 < \theta < 30°$ ($0 \le h \le 14$, $0 \le k \le 26$, $0 \le l \le 10$), ω–2θ scan mode. Two standard reflexions ($\bar{1}50$; 150), variation in intensity < 2% of mean value. 2438 independent reflexions measured, 770 unobserved [$I < 2\sigma(I)$]. Lorentz and polarization correction, no correction for absorption ($\mu R \sim 0{\cdot}12$) or extinction. Patterson function and heavy-atom method with initial set of phases based on Br and S atom positions. Full-matrix least-squares refinement on F, anisotropic. Difference Fourier synthesis revealed H-atom positions; isotropic temperature factor $B = 4{\cdot}0$ Å^2 for H atoms. Further least-squares refinement including positional parameters of H atoms and anomalous-dispersion correction for Br and S atomic scattering factors (*International Tables for*

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* IUPAC name: 1-{6-acetoxy-3-(*p*-bromophenyl)-1-ethyl-2-thioxo-2,3,3a,5,6,6a-1*H*-furo[2,3-*d*]imidazol-5-yl}ethylene diacetate.

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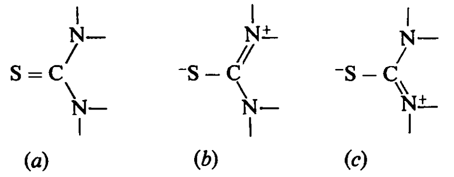
X-ray Crystallography, 1974) reduced wR to 0·069 ($R = 0{\cdot}089$). The enantiomorphic form of the molecule was refined separately and converged to a final wR of 0·052 ($R = 0{\cdot}070$); weighting scheme based on statistical count criterion ($w = 1/\sigma_F^2$). $(\Delta/\sigma)_{\max} = 0{\cdot}07$, $S = 1{\cdot}52$, 364 refined parameters. Number of reflexions/number of parameters = 4·5. Final difference synthesis showed $0{\cdot}25 > \Delta\rho > -0{\cdot}20$ e Å^{-3}. Application of $\mathscr{R}$ test (Hamilton, 1965) indicated that the enantiomorph is correct to a significance level much lower than 0·005 [$wR(1)/wR(2) = 1{\cdot}325$; $\mathscr{R}_{1,1668,0.005} \simeq 1{\cdot}003$] and therefore can be retained as the structural chirality. Moreover, this configuration is consistent with that defined by reference to the sugar moiety (Galbis-Pérez *et al.*, 1984). 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 listed in Table 1.* Atom numbering and bond lengths and angles involving non-hydrogen atoms are given in Fig. 1.

Molecular geometry

Bond distances and angles in the imidazolidine ring agree with the mean values reported for analogous glycofuranosoimidazolidine-2-thione compounds (Estrada, Conde & Márquez, 1983, 1984; Conde, Millan, Conde & Márquez, 1985*a*,*b*). The S—C bond length of 1·653 (11) Å and those observed for N(1)—C(1) = 1·356 (14) and N(2)—C(1) = 1·350 (13) Å indicate the contribution of the canonical resonance forms of the thiourea system:



The title compound does not show asymmetry of the endocyclic N—C bonds found in analogous compounds and attributed to the different substituents at the two N atoms. The imidazolidine ring is nearly planar: deviations of the ring atoms from the least-squares plane are lower than 2σ [$\sum(\Delta/\sigma)^2 = 8{\cdot}26$, χ^2 at 95% = 5·99]. The phenyl ring forms a dihedral angle of 60·6 (4)° with the imidazolidine ring. Values in the range 40–80° were found for analogous compounds, and indicate a significant contribution of intramolecular potential energy (phenyl–imidazolidine) over intermolecular. 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) = 91·6 (13)°.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos(\mathbf{a}_i,\mathbf{a}_j).$$

	x	y	z	$U_{\rm eq}$
Br	0·9463 (1)	0·1622 (1)	1·0959 (1)	59 (1)
S	0·7331 (2)	0·2059 (1)	0·3663 (3)	51 (1)
O(1)	0·4650 (5)	0·1238 (3)	0·7141 (6)	38 (3)
O(2)	0·2604 (5)	0·1227 (3)	0·5532 (7)	43 (3)
O(4)	0·3797 (6)	−0·0180 (3)	0·5568 (8)	52 (3)
O(5)	0·5711 (7)	−0·0052 (3)	0·7441 (8)	56 (3)
O(6)	0·1886 (6)	0·1500 (4)	0·3302 (8)	69 (4)
O(8)	0·2051 (6)	−0·0345 (4)	0·6310 (12)	10 (5)
O(9)	0·6178 (8)	−0·0337 (5)	0·9768 (9)	99 (5)
N(1)	0·5967 (6)	0·1895 (3)	0·6050 (10)	37 (3)
N(2)	0·5153 (7)	0·1858 (4)	0·3851 (9)	41 (3)
C(1)	0·6145 (9)	0·1925 (5)	0·4538 (12)	39 (4)
C(2)	0·4817 (8)	0·1802 (4)	0·6467 (11)	35 (4)
C(3)	0·4209 (8)	0·1795 (5)	0·4887 (12)	40 (4)
C(4)	0·3694 (8)	0·1173 (5)	0·4884 (12)	39 (4)
C(5)	0·4424 (9)	0·0815 (4)	0·5955 (11)	39 (4)
C(7)	0·3910 (9)	0·0279 (5)	0·6699 (12)	43 (4)
C(8)	0·4608 (9)	0·0039 (5)	0·7986 (12)	52 (5)
C(9)	0·6850 (8)	0·1831 (5)	0·7175 (12)	38 (4)
C(10)	0·7564 (10)	0·1379 (5)	0·7069 (13)	51 (5)
C(11)	0·8370 (9)	0·1312 (5)	0·8221 (15)	54 (5)
C(12)	0·8362 (8)	0·1710 (6)	0·9408 (12)	47 (5)
C(13)	0·7619 (9)	0·2170 (5)	0·9508 (12)	45 (6)
C(14)	0·6845 (8)	0·2236 (5)	0·8376 (13)	41 (4)
C(15)	0·4932 (10)	0·1987 (6)	0·2245 (13)	64 (5)
C(16)	0·5090 (11)	0·1451 (6)	0·1280 (13)	83 (6)
C(17)	0·1768 (9)	0·1388 (5)	0·4621 (13)	52 (5)
C(18)	0·0711 (8)	0·1457 (5)	0·5444 (13)	56 (5)
C(21)	0·2812 (9)	−0·0469 (6)	0·5531 (14)	59 (5)
C(22)	0·2888 (11)	−0·0994 (6)	0·4503 (15)	79 (6)
C(23)	0·6433 (9)	−0·0255 (5)	0·8467 (15)	63 (5)
C(24)	0·7566 (11)	−0·0345 (6)	0·7840 (17)	88 (7)

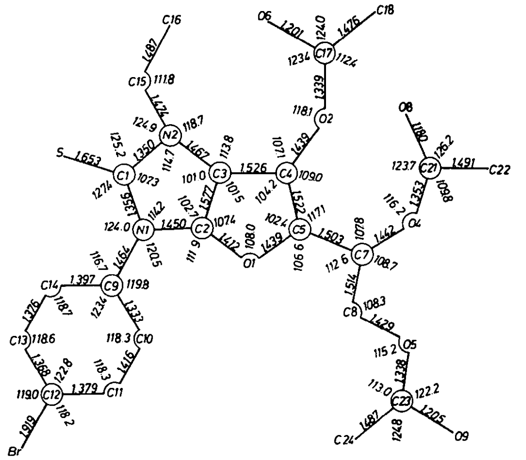


Fig. 1. Bond lengths (Å) and angles (°). Standard deviations are in the ranges 0·01–0·02 Å and 0·7–0·9°, respectively.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42636 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles in the furanosyl ring are close to the mean values observed for analogous compounds. The asymmetry of the endocyclic bonds O(1)—C(2) = 1·412 (12) and O(1)—C(5) = 1·439 (11) Å, a typical feature of these compounds due to anomeric effects, is difficult to establish in this case because of the high e.s.d.'s. ($\Delta/\sigma = 1{\cdot}66$). The furanose ring is not planar as shown by the deviations from the least-squares plane through the five atoms of the ring ($\Delta/\sigma > 6$). In terms of the ring-puckering coordinates (Cremer & Pople, 1975), the amplitude and phase magnitudes are $Q = 0{\cdot}382$ (9) Å and $\varphi = 140$ (1)° for the sequence O(1)—C(2)—C(3)—C(4)—C(5) and the resulting conformation is near to the puckering mode ^4E, as found for analogous compounds (Estrada, Conde & Márquez, 1984; Conde, Millan, Conde & Márquez, 1985*b*). The values of the pseudorotational parameters correspond to one of the zones of high population density in the conformational wheel defined in a statistical study, performed over a large number of sugar rings by Murray-Rust & Motherwell (1978). The asymmetry parameter of Nardelli (1983*a*), $\Delta C_s[C(5)] = 0{\cdot}019$ (5), indicates an approximate mirror symmetry in the ring. The small value of the torsion angle O(1)—C(2)—C(3)—C(4) = 1·8 (10)°, a typical feature of these compounds, may be attributed to the distortion of the furanose group on its fusion with the imidazolidine ring.

The two fused rings in the bicyclic system show a *cis* form of coupling and the bonds at C(2) and C(3) are nearly eclipsed, these features being similar to those observed for analogous compounds. The dihedral angle between the least-squares planes through the imidazolidine and furanose rings is 71·1 (4)°.

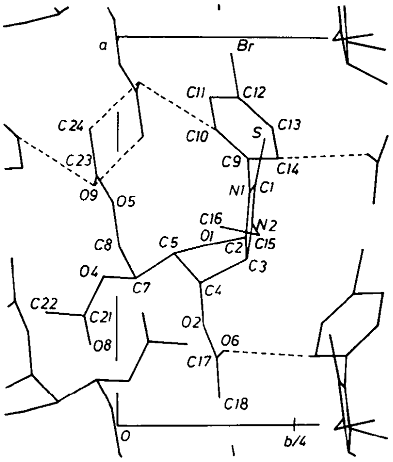

Fig. 2. A view of the unit cell along [001].

Crystal-packing analysis

Fig. 2 shows the contents of the unit cell viewed down [001]. The crystal cohesion is due mainly to van der Waals forces. Only the interactions C(10)—H(10)···O(9) ($-x+\frac{3}{2}$, $-y$, $z-\frac{1}{2}$) and C(24)—H(242)···O(9) ($-x+\frac{3}{2}$, $-y$, $z-\frac{1}{2}$), linking molecules related by a screw axis parallel to [001], and C(14)—H(14)···O(6) ($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+1$), between molecules related by a screw axis parallel to [100], may be considered as possible hydrogen bonds. Details of the geometry of these contacts are: C(10)—H(10) = 1·05 (6), C(10)···O(9) = 3·45 (1), H(10)···O(9) = 2·56 (6) Å, C(10)—H(10)···O(9) = 142 (4)°; C(24)—H(242) = 1·05 (12), C(24)···O(9) = 3·46 (2), H(242)···O(9) = 2·70 (12) Å, C(24)—H(242)···O(9) = 129 (8)°; C(14)···O(6) = 3·20 (1), H(14)···O(6) = 2·68 (5) Å, C(14)—H(14)···O(6) = 112 (4)°. As observed, the H···O distances of these contacts are close to the sum of the van der Waals radii of H and O (1·20 and 1·50 Å) and the angle C—H···O has a low value. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii have been detected. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983*b*).

A minimization of the crystal lattice energy with respect to lattice constants, molecular translation and rotation and also subrotation of molecular fragments about selected bonds as axes was performed by means of the program *PCK*6 (Williams, 1972*b*, 1974) starting from the experimental structure. Potential functions in the form $U(r) = -Ar^{-6} + B\exp(-Cr)$ were used to represent the non-bonded interatomic potential energy. The set of potential parameters included parameters fitted by Williams (1972*a*) for C···C and H···H interactions, by Govers (1975) for N···N, by Mason & Kreevoy (1955) for O···O and S···S and parameters of Burgos & Bonadeo (1977) for Br···Br. For mixed interactions, combination rules of Mirskaya (1973) were used.

Three runs of energy minimization were carried out: in the first, the X-ray molecular structure was retained and the lattice constants were fixed; in the second, cell parameters were included as variables and, finally, five subrotations about selected bonds as axes were relaxed.

Representative reults of energy minimization are given in Table 2. The calculated value for lattice energy, not included in Table 2, is higher than the real one because of the representation of intermolecular hydrogen bonds by van der Waals potential functions. As shown in Table 2, the inclusion of the cell parameters as variables leads to a contraction along **b** (0·7%) and **c** (0·2%) but an expansion is observed along **a** (2·8%). Similar results are obtained if experimental coordinates of hydrogen atoms are substituted by those calculated from expected geometry. This unexpected expansion of the cell cannot be related simply to the omission of the electrostatic interactions and the description of the

Table 2. *Molecular-packing analysis*

(*a*) With cell parameters and torques fixed at experimental values (*); (*b*) with optimized cell parameters and torques fixed; (*c*) with cell parameters fixed and torques relaxed.

	(*a*)	(*b*)	(*c*)
Cell parameters			
a (Å)	12·056 (7)*	12·398	12·056*
b (Å)	22·420 (8)*	22·255	22·420*
c (Å)	8·841 (2)*	8·820	8·841*
V (Å^3)	2390 (2)*	2433	2390*
Molecular parameters			
Translation (Å)	0·31	0·19	0·12
Rotation (°)	0·51	0·57	0·99
Subrotations (°)			
C(2)–N(1)–C(9)–C(10)	111 (1)*	111*	116
C(1)–N(2)–C(15)–C(16)	92 (1)*	92*	74
C(3)–C(4)–O(2)–C(17)	85 (1)*	85*	76
C(5)–C(7)–O(4)–C(21)	−134 (1)*	−134*	−152
C(5)–C(7)–C(8)–O(5)	−52 (1)	−52*	−48

hydrogen bonds by van der Waals potential functions; rather, it should indicate an inherent limitation of the energy sets based on experimental data at room temperature, owing to the nonuniform effect of temperature on the unit-cell parameters: it is different in different crystals and it is different for different cell parameters of the same crystal (anisotropy in the thermal expansion coefficients).

Apart from this effect, the theoretical configuration agrees with the experimental structure. The optimized structure remains very similar with regard to the molecular parameters as shown in Table 2: shifts of positional and orientational molecular parameters are lower than 0·3 Å and 1° respectively. The torsional angles of selected molecular fragments show in two cases (the ethyl group and one of the acetyl chains) a large distortion and this could be attributed to the presence of intramolecular contacts with hydrogen-bond character linking the different rotational groups in the molecule.

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References

Burgos, E. & Bonadeo, H. (1977). *Chem Phys. Lett.* **49**, 475–478.

Conde, C. F., Millan, M., Conde, A. & Márquez, R. (1985*a*). *Acta Cryst.* C**41**, 277–280.

Conde, C. F., Millan, M., Conde, A. & Márquez, R. (1985*b*). *Acta Cryst.* C**41**. 1658–1662.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Estrada, M. D., Conde, A. & Márquez, R. (1983). *Acta Cryst.* C**39**, 1418–1421.

Estrada. M. D., Conde, A. & Márquez, R. (1984). *Acta Cryst.* C**40**, 898–901.

Galbis Pérez, J. A., Palacios Albarrán, J. C., Jiménez Requejo, J. L. & Avalos González, M. (1984). *Carbohydr. Res.* **129**, 131–142.

Govers, H. A. J. (1975). *Acta Cryst.* A**31**, 380–385.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Mason, E. A. & Kreevoy, M. M. (1955). *J. Am. Chem. Soc.* **77**, 5808–5814.

Mirskaya, K. V. (1973). *Tetrahedron*, **29**, 679–682.

Murray-Rust, P. & Motherwell, S. (1978). *Acta Cryst.* B**34**, 2534–2546.

Nardelli, M. (1983*a*). *Acta Cryst.* C**39**, 1141–1142.

Nardelli, M. (1983*b*). *Comput. Chem.* **7**, 95–98.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The *XRAY* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Williams, D. E. (1972*a*). *Acta Cryst.* A**28**, 84–88.

Williams, D. E. (1972*b*). *Acta Cryst.* A**28**, 629–635.

Williams, D. E. (1974). *Acta Cryst.* A**30**, 71–77.

Acta Cryst. (1986). C**42**, 457–462

Structure of *N*-Aromatic Amides. II. XC_6H_4NHCOY*

By Setsuo Kashino, Toshiko Matsushita, Tetsuyuki Iwamoto, Katsuji Yamaguchi and Masao Haisa

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, *Japan*

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Abstract. $T = 296$ K, Cu $K\alpha$, $\lambda = 1·5418$ Å. (1) Salicylanilide ($X = $ H, $Y = o$-HOC_6H_4), $C_{13}H_{11}NO_2$, $M_r = 213·23$, m.p. = 406·5–407·5 K, orthorhombic, *Pbca*, $a = 11·018$ (2), $b = 24·781$ (5), $c = 7·760$ (1) Å, $V = 2118·7$ (5) Å^3, $Z = 8$, $D_m = 1·33$, $D_x = 1·337$ Mg m^{-3}, $\mu = 0·70$ mm^{-1}, $F(000) = 896$, $R = 0·050$ for 1577 unique reflections. (2) *o*-Nitroacetanilide ($X = o$-NO_2, $Y = CH_3$), $C_8H_8N_2O_3$, $M_r = 180·16$, m.p. = 364–367 K, monoclinic, $P2_1/n$, $a = 15·507$ (3), $b = 4·9576$ (5), $c = 10·924$ (2) Å, $\beta = 97·68$ (1)°, *V*

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* Part I: Haisa, Kashino, Ueno, Shinozaki & Matsuzaki (1980).

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