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Note

Crystal and molecular structure of 1-phenyl-(1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidine-2-selone *

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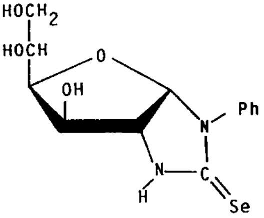
1-Phenyl-(1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidine-2-selone (**1**) was prepared[1] from 2-amino-2-deoxy-D-glucose hydrochloride and phenyl isoselenocyanate.



1

In order to establish possible correlations between spectroscopic data[1] and X-ray single-crystal diffractometry data, the crystal structure of **1** has been determined. The crystal structure of the 1-*p*-bromophenyl analogue has been reported[1].

The positional and isotropic thermal parameters for the non-hydrogen atoms of **1** are given in Table I, and the bond lengths and angles in Table II. The mean C–H distance is 1.08 Å and the O–H distance 1.00 Å. The mean value of C–C in the phenyl group is 1.387(12) Å. The bond lengths and angles in the glucofurano[2,1-*d*]imidazolidine-2-selone moiety are normal except for the C–C bonds which are rather longer than the normal C(sp^3)–C(sp^3) single bond.

The asymmetric endocyclic C–O bond lengths, C-1–O 1.406(8) and C-4–O 1.443(7) Å, show clearly the anomeric effect. The Se–C bond length of 1.844(6) Å is intermediate between those of an Se–C single (1.98 Å) and double bond (1.67

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TABLE I

Atomic coordinates and thermal parameters for non-H atoms

Atom	x/a	y/b	z/c	U_{eq} [a]
Se	0.38285(5)	0.85085(5)	0.66633(7)	360(2)
O	0.4742(3)	0.9698(3)	1.1511(4)	360(13)
N-3	0.5272(4)	0.9894(4)	0.8177(5)	354(15)
O-6	0.6258(4)	0.8151(4)	1.4818(5)	541(17)
C-4	0.5900(4)	0.9308(4)	1.1238(6)	299(16)
O-5	0.7678(3)	0.8832(3)	1.2375(5)	412(14)
C-6	0.5843(6)	0.8248(5)	1.3423(7)	417(19)
C-21	0.4301(5)	0.9322(4)	0.8151(6)	314(16)
O-3	0.6803(5)	1.1036(4)	1.1201(6)	555(18)
C-3	0.6436(5)	1.0181(5)	1.0347(7)	364(18)
C-5	0.6488(5)	0.9102(5)	1.2639(7)	347(17)
C-2	0.5390(5)	1.0514(4)	0.9443(7)	341(17)
N-1	0.3737(4)	0.9428(3)	0.9366(5)	312(14)
C-1	0.4317(5)	1.0185(4)	1.0298(7)	358(18)
C-511	0.1503(7)	0.7954(6)	1.1368(8)	535(24)
C-611	0.2599(6)	0.8313(6)	1.0921(8)	474(22)
C-211	0.1640(5)	0.9247(5)	0.9049(8)	382(19)
C-111	0.2641(5)	0.8985(4)	0.9753(6)	300(16)
C-411	0.0522(6)	0.8215(5)	1.0656(9)	483(24)
C-311	0.0575(5)	0.8859(6)	0.9490(10)	496(25)

[a] $U_{eq} = \frac{1}{3}\Sigma[U_{ij}a_i^*a_j^*a_ia_j\cos(a_ia_j)]\times 10^4$.

Å). This partial double-bond character reflects the resonance of the selenourea system.

The phenyl and imidazolidine groups are planar and the maximum deviations from the least-squares planes are 0.014(8) and 0.017(5) Å, respectively. The Se

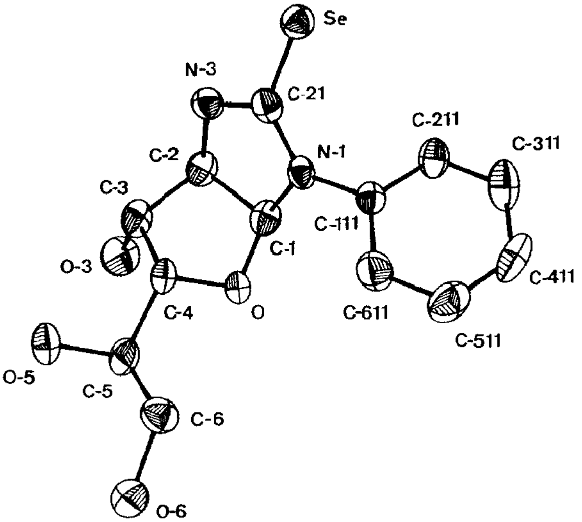

Fig. 1. An ORTEP view of **1** showing the atomic numbering. Thermal ellipsoids enclose 50% probability.

TABLE II

Bond lengths (Å) and angles (°)

Bond length		Angles	
Se–C-21	1.843(6)	C-4–O–C-1	108.5(4)
O–C-4	1.442(6)	C-21–N-3–C-2	112.7(5)
O–C-1	1.406(8)	O–C-4–C-5	107.7(4)
N-3–C-21	1.329(7)	O–C-4–C-3	103.1(4)
N-3–C-2	1.454(8)	C-3–C-4–C-5	116.0(5)
O-6–C-6	1.429(8)	O-6–C-6–C-5	111.4(5)
C-4–C-3	1.527(8)	Se–C-21–N-3	124.3(4)
C-4–C-5	1.530(8)	N-3–C-21–N-1	109.5(5)
O-5–C-5	1.430(7)	Se–C-21–N-1	126.1(4)
C-6–C-5	1.510(9)	C-4–C-3–O-3	110.1(5)
C-21–N-1	1.342(8)	O-3–C-3–C-2	110.5(5)
O-3–C-3	1.420(8)	C-4–C-3–C-2	101.4(4)
C-3–C-2	1.541(9)	O-5–C-5–C-6	112.8(5)
C-2–C-1	1.538(9)	C-4–C-5–C-6	110.1(5)
N-1–C-1	1.469(8)	C-4–C-5–O-5	107.8(5)
N-1–C-111	1.428(7)	N-3–C-2–C-3	113.5(5)
C-511–C-611	1.405(1)	C-3–C-2–C-1	104.4(5)
C-511–C-411	1.360(11)	N-3–C-2–C-1	103.1(5)
C-611–C-111	1.408(10)	C-21–N-1–C-111	127.8(5)
C-211–C-111	1.374(9)	C-21–N-1–C-1	112.1(4)
C-211–C-311	1.385(9)	C-1–N-1–C-111	119.7(5)
C-411–C-311	1.386(12)	C-2–C-1–N-1	102.2(5)
		O–C-1–N-1	112.3(5)
		O–C-1–C-2	106.4(5)
		C-611–C-511–C-411	120.7(7)
		C-511–C-611–C-111	117.9(6)
		C-111–C-211–C-311	120.1(6)
		C-611–C-111–C-211	120.6(6)
		N-1–C-111–C-211	120.9(5)
		N-1–C-111–C-611	118.3(5)
		C-511–C-411–C-311	120.8(7)
		C-211–C-311–C-411	119.6(6)

atom is at 0.105(1) Å from the respective ring mean-square plane of the ring. The furanose ring is not planar and the ring-puckering coordinates[2] are amplitude $Q = 0.378(6)$ Å and phase $\phi = 104.1(9)°$ for the sequence C-1–C-2–C-3–C-4–O. The asymmetry parameters[3] are ΔC_s(C-4) = 0.017(3) and ΔC_2(C-1) = 0.058(2), so that the conformation is an envelope with a pseudo-mirror plane through C-4. The endocyclic torsion angles are C-4–O–C-1–C-2 −23.5(6)°, O–C-1–C-2–C-3 −1.6(7)°, C-1–C-2–C-3–C-4 −23.9(6)°, C-2–C-3–C-4–O −37.8(6)°, and C-3–C-4–O–C-1 39.4(6)°, O-3 is axial and C-5 is quasi-equatorial, and the angles between planes are furan–imidazolidine 108.6(2)°, phenylimidazolidine 115.4(2)°, and phenylfuran 13.5(2)°.

Fig. 1 shows an Ortep[4] view with the atomic numbering, and the Newman projection along the C-5–C-6 bond is shown in Fig. 2. The packing is governed by van der Waals forces. There is one short intramolecular contact between one C

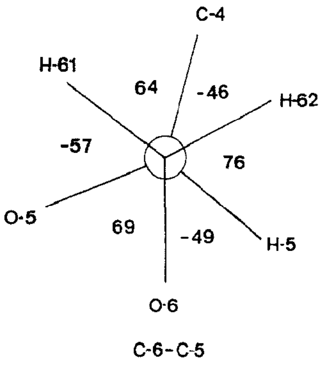

Fig. 2. The Newman projection along C-5–C-6 bond of **1**.

(phenyl) and the oxygen of the furanose ring, C-611 · · · O = 3.073(9) Å and C-611–H-611 · · · O = 105.7(4)°.

There are significant differences between the crystal and molecular structures of the 1-phenyl (**1**) and 1-*p*-bromophenyl derivatives. The geometries of the molecules are similar, although the intramolecular H-bond found for the 1-phenyl derivative **1** is only an intramolecular contact [3.23(3) Å] for the 1-*p*-bromophenyl analogue. The crystal cohesions for the structures are different since the Br substituent increases the cell volume; in addition, the packing for the 1-phenyl derivative **1** is governed by van der Waals forces, whereas, in the 1-*p*-bromophenyl derivative, the molecules are linked by many H-bonds.

EXPERIMENTAL *

A prismatic single crystal with approximate dimensions 0.12 × 0.63 × 0.10 mm and well-shaped faces was used. Preliminary Weissenberg photographs indicated that the crystal belonged to the orthorhombic system with systematic absences consistent with $P2_12_12_1$.

Unit-cell parameters, obtained from a least-squares fitting of the setting angles for 25 reflections in the range $5 < \theta < 16°$, were $a = 11.489(2)$, $b = 12.627(1)$, $c = 9.618(1)$ Å, and $Z = 4$. The unit-cell volume V was 1395.3(2) Å^3, the absorption coefficient μ was 2.67 mm^{-1}, $D_c = 1.63$ Mg m^{-3}, D_m measured by flotation = 1.64 Mg m^{-3}, and $F(000) = 696$.

An Enraf–Nonius CAD-4 diffractometer was used with monochromated Mo$K\alpha$ radiation (0.7107 Å) and an $\omega/2\theta$ scan technique at room temperature ($h \leqslant 14$, $k \leqslant 15$, $l \leqslant 11$). Three reference reflections (1 4 0, 1 4 $\bar{1}$, and 1 4 1), monitored

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* Lists of the hydrogen co-ordinates, thermal parameters, and structure amplitudes are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/528/*Carbohydr. Res.*, 242 (1993) 265–269.

every 100 reflections, showed only statistical fluctuations. No significant changes in the intensities were noted. From 1607 measured reflections, 1309 were observed with $I \geqslant 2\sigma(I)$. Corrections were made for Lorentz-polarisation effects but not for extinction, and an empirical absorption correction following the DIFABS procedure[5] was applied to isotropically refined data. The structure was solved by Patterson techniques (Se atom) and the remaining non-H atoms from a single cycle of DIRDIF[6]. After anisotropic refinement by full-matrix least squares of all of the 20 non-H atoms in the asymmetric unit, the H atoms were assigned the same isotropic thermal parameters as the atoms to which they were bonded and were included but not refined in the final stage of refinement.

Refinement was based on F (structure amplitudes) to minimise the function $\Sigma\omega(|F_o| - |F_0|)^2$ with $\omega = 1/\sigma^2(F_o)$, and 181 parameters were refined (9 parameters per atom plus 1 for the scale); the over-determination ratio was 8.0 reflections/parameter. The refinement led to a final convergence with $R = 0.031$ and $\omega R = 0.041$. The maximum shift/error was < 0.07 except for the x-coordinate of N-1, and the goodness-of-fit parameter $S = 0.922$. Max and min heights in the final difference Fourier synthesis were 0.3 and -0.3 e Å^{-3}.

Atomic scattering factors were taken from the International Tables for X-ray Crystallography[7], and all calculations were carried out with the X-ray System of crystallographic programs[8]. Bond lengths (Å) and angles (°) were calculated by the program PARST, written by Nardelli[9].

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REFERENCES

1 J. Fernández-Bolaños Guzmán, T. Skrydstrup, A. López-Castro, M.J. Diánez Millán and M.D. Estrada de Oya, *Carbohydr. Res.,* 237 (1992) 303–311.
2 D. Cremer and J.A. Pople, *J. Am. Chem. Soc.,* 97 (1975) 1354–1358.
3 M. Nardelli, *Acta Crystallogr., Sect. C,* 39 (1983) 1141–1142.
4 C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.
5 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A,* 39 (1983) 158–166.
6 P.T. Beursken, W.P. Bosman, H.M. Doesburg, R.O. Gould, Th.E.M. van der Hark, P.A.J. Prick, J.H. Noordik, G. Beurskens, V. Parthasarathi, H.J. Bruins Slot, and R.C. Haltiwanger, DIRDIF, Direct Methods for Difference Structures. An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors, Tech. Rep. 1984/1, Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands, 1984.
7 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
8 J.M. Stewart, F.A. Kundell, and J.C. Baldwin, The X-ray System 70, Computer Science Center, University of Maryland, College Park, 1970.
9 M. Nardelli, *J. Comput. Chem,* 7 (1983) 95–98.