References

Bolt, C. C. & Zeelen, J. F. (1973). *Rec. Trav. Chim. Pays-Bas*, **92**, 1267–1271.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. Ibers & W. C. Hamilton, Table 2.2B. Birmingham: Kynoch Press.

Duax, W. L., Cody, V., Griffin, J. F., Rohrer, D. C. & Weeks, C. M. (1978). *J. Toxicol. Environ. Health*, **4**, 205–227.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. I. New York: IFI/Plenum.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–383. New York: John Wiley.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kirk, D. N. & Hartshorn, M. P. (1968). *Steroid Reaction Mechanism*, p. 196. Amsterdam: Elsevier.

Mori, H. M. (1962). *Chem. Pharm. Bull.* **10**, 386–390.

Rendle, D. F. & Trotter, J. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 847–852.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.

3,4,6-Tri-*O*-acetyl-1,2-dideoxy-D-hex-1-enopyranose*

By J. W. Krajewski, Z. Urbanczyk-Lipkowska and P. Gluzinski

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

and J. Bleidelis and A. Kemme

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga, USSR

Abstract. $C_{12}H_{16}O_7$, $M_r = 272 \cdot 2$, $F(000) = 576$, orthorhombic, $P2_12_12_1$, $a = 5 \cdot 215$ (1), $b = 15 \cdot 485$ (2), $c = 16 \cdot 446$ (2) Å, $V = 1328 \cdot 1$ Å^3, $Z = 4$, $D_x = 1 \cdot 33$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·98 mm^{-1}. The structure was solved by direct methods. The final R and R_w values were 0·059 and 0·043 respectively (weights from counting statistics). The six-membered hetero-ring of the molecule is characterized by the half-chair conformation $^4H_5$.

Introduction. The title compound (GLUCAL) is one of a series of unsaturated monosaccharides. GLUCAL is widely used in preparative carbohydrate chemistry. It represents a trisubstituted 3,4-dihydro-2*H*-pyran whose conformation is of interest in conformational analysis. Colorless crystals were obtained by recrystallization from diethyl ether–petroleum ether solution. The space group was determined from photographs. Cell dimensions and reflection intensities were measured on a Syntex $P2_1$ diffractometer (Institute of Organic Synthesis, Riga, USSR) with graphite-monochromated Cu $K\alpha$ radiation. Of the 1473 independent reflections ($2\theta < 150°$), 1121 had intensities greater than $2\sigma_{(I)}$. No

correction for absorption was made. The structure was solved with the *MULTAN XTL* program (SuperNova Computer, Riga). At this stage, full-matrix least-squares refinement [program *CRYLSQ* in the XRAY 70 system (Stewart, Kundell & Baldwin, 1970), performed on a CDC Cyber-73 Computer, Warsaw] with individual isotropic temperature factors led to $R = 0 \cdot 158$ and $R_w = 0 \cdot 110$ [$w = 1/\sigma_{(F_o)}^2$]. The scattering factors used were those given in *International Tables for X-ray Crystallography* (1974). Several cycles of refinement with anisotropic thermal coefficients (and weights as above) were then performed. The final R and R_w values after inclusion of the geometrically calculated H coordinates were 0·059 and 0·043 respectively. The average shift/error value was 0·0015 (maximum = 0·0102). The final coordinates of the non-hydrogen atoms are listed in Table 1.†

Discussion. The six-membered hetero-ring of GLUCAL with a C(1)=C(2) double bond (Fig. 1) has

---

* For a preliminary account see Krajewski, Urbanczyk-Lipkowska, Gluzinski, Bleidelis & Kemme (1978).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34103 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
C(1)	−2782 (10)	775 (4)	10441 (3)
C(2)	−2898 (11)	1421 (3)	9927 (3)
C(3)	−1490 (11)	1399 (3)	9131 (3)
C(4)	−608 (10)	491 (3)	8959 (3)
C(5)	597 (10)	121 (3)	9731 (3)
O(1)	−1323 (7)	51 (2)	10351 (2)
C(6)	1691 (11)	−762 (3)	9597 (3)
C(7)	4957 (12)	−1568 (3)	10246 (4)
C(8)	6055 (13)	−1784 (3)	11053 (3)
C(9)	−3581 (12)	2491 (4)	8360 (3)
C(10)	−5509 (14)	2656 (4)	7716 (3)
C(11)	1125 (12)	−36 (4)	7708 (3)
C(12)	3314 (11)	66 (4)	7150 (3)
O(2)	−3199 (7)	1633 (2)	8477 (2)
O(3)	1288 (7)	530 (2)	8335 (2)
O(4)	2963 (7)	−1017 (2)	10331 (2)
O(5)	5701 (8)	−1816 (2)	9601 (2)
O(6)	−2498 (9)	3021 (2)	8763 (2)
O(7)	−554 (9)	−559 (3)	7663 (3)

Fig. 1. *ORTEP* diagram of the molecule. Thermal-motion ellipsoids are at the 40% probability level.

Table 2. *Least-squares planes*

The equations of the planes are of the form $Px + Qy + Rz = S$, where x, y and z are in Å in orthogonal space.

Plane	Atoms defining the plane or line	P	Q	R	S
P1	O(1), C(1) C(2), C(3)	0·7775	0·4492	0·4401	6·9840
P2	C(3), O(2) C(9), O(6)	−0·7660	−0·0090	0·6428	10·2238
P3	C(4), O(3) C(11), O(7)	−0·5636	0·6530	−0·5059	−6·7785
P4	C(6), O(4) C(7), O(5)	0·6167	0·7839	−0·0718	−1·5104

Line	Line	Line	
L1	C(3), O(2)	L3	C(5), C(6)
L2	C(4), O(3)	L4	C(6), O(4)

Distances of atoms from the planes (Å)

Plane 1		Plane 2		Plane 3		Plane 4	
O(1)	0·007	C(3)	0·004	C(4)	0·000	C(6)	−0·004
C(1)	−0·015	O(2)	−0·008	O(3)	0·001	O(4)	0·008
C(2)	0·014	C(9)	0·009	C(11)	−0·001	C(7)	−0·010
C(3)	−0·006	O(6)	−0·005	O(7)	0·001	O(5)	0·005
C(4)	−0·404						
C(5)	0·386						
C(6)	0·120						
O(2)	−1·010						
O(3)	−0·060						
O(4)	0·990						

Angles between the planes (°)

$$P(1)-P(2) = 72, P(1)-P(3) = 69, P(1)-P(4) = 37$$

Angles between the lines and their projections on the planes (°)

$$P(1)-L(1) = 136, P(1)-L(2) = 166, P(1)-L(3) = 170, P(1)-L(4) = 143$$

the half-chair conformation $^4H_5$ [for nomenclature see Schwartz (1973)]. The asymmetry parameter (Duax & Norton, 1975), calculated from ring torsion angles, is $\Delta C_2^{1-2} = 1·70°$. When compared with those of other unsaturated sugars (Krajewski, Urbanczyk-Lipkowska, Gluzinski, Bleidelis & Kemme, 1978; Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1979) it has the lowest value. This seems to be because in this case the atoms lying above and below the O(1)—C(1)—C(2)—C(3) least-squares plane (referred to below as the ring plane) are both C(sp^3) atoms [C(4) and C(5)]. Their distances from this plane are −0·404 and 0·386 Å respectively (Table 2) (according to the IUPAC numbering rule the signs should be interchanged). Cesario, Guilhem & Martin (1977) investigated the tri-O-benzyl-D-glucal molecule with the $^4H_5$ ring conformation. They found the C(4) and C(5) deviations from the ring plane to be +0·32 and −0·40 Å respectively. Thus, it may be concluded that the half-chair deformation in the tri-O-benzyl derivative is greater than in the present case. No other data have been found in the literature. The pseudoequatorial acetoxymethyl substituent at C(5) deviates below the ring plane. Table 2 gives the deviations from the ring plane for atoms in the substituents at C(3) and C(4). These deviations for O(2) and O(3) (Fig. 1) were found to be −1·01 and −0·60 Å respectively. The angles formed by the C(3)—O(2) and C(4)—O(3) bonds (lines L1 and L2, Table 2) with the ring plane determined the positions of both substituents as pseudo-equatorial with the O-acetyl groups deviating in the same direction.

The bond lengths and bond angles of the GLUCAL molecule are listed in Tables 3 and 4. The ring geometry is similar, in general, to those reported earlier
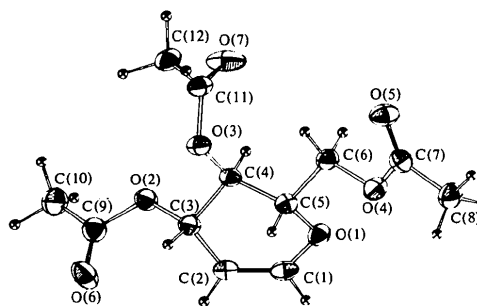
Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

O(1)—C(1)	1·364 (6)	C(4)—O(3)	1·427 (6)
C(1)—C(2)	1·311 (7)	O(3)—C(11)	1·356 (6)
C(2)—C(3)	1·501 (7)	C(11)—O(7)	1·195 (7)
C(3)—C(4)	1·505 (7)	C(11)—C(12)	1·474 (8)
C(4)—C(5)	1·528 (6)	C(5)—C(6)	1·498 (7)
C(5)—O(1)	1·433 (6)	C(6)—O(4)	1·432 (6)
C(3)—O(2)	1·443 (6)	O(4)—C(7)	1·353 (7)
O(2)—C(9)	1·357 (6)	C(7)—C(8)	1·483 (8)
C(9)—O(6)	1·197 (7)	C(7)—O(5)	1·193 (7)
C(9)—C(10)	1·483 (9)		

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

O(1)–C(1)–C(2)	125·7 (5)	O(3)–C(4)–C(5)	109·2 (4)
C(1)–C(2)–C(3)	121·5 (5)	C(4)–O(3)–C(11)	118·5 (4)
C(2)–C(3)–C(4)	109·5 (4)	O(3)–C(11)–C(12)	110·9 (5)
C(3)–C(4)–C(5)	108·7 (4)	O(3)–C(11)–O(7)	122·0 (5)
C(4)–C(5)–O(1)	109·4 (4)	O(7)–C(11)–C(12)	127·0 (5)
C(5)–O(1)–C(1)	113·8 (4)	C(4)–C(5)–C(6)	112·1 (4)
C(2)–C(3)–O(2)	110·0 (5)	O(1)–C(5)–C(6)	107·5 (4)
O(2)–C(3)–C(4)	106·5 (4)	C(5)–C(6)–O(4)	107·7 (4)
C(3)–O(2)–C(9)	116·3 (4)	C(6)–O(4)–C(7)	116·3 (4)
O(2)–C(9)–O(6)	121·6 (5)	O(4)–C(7)–O(5)	123·0 (5)
O(2)–C(9)–C(10)	111·7 (5)	O(4)–C(7)–C(8)	110·3 (5)
O(6)–C(9)–C(10)	126·7 (5)	C(8)–C(7)–O(5)	126·7 (6)
C(3)–C(4)–O(3)	107·9 (4)		

for other unsaturated sugars (López de Lerma, Martínez-Carrera & García-Blanco, 1973; Stokhuyzen & Chung Chieh, 1976; Gould, Gould, Rees & Wight, 1976). The bond lengths are: $C(sp^2)$–$C(sp^2)$ 1·311 (7), $C(sp^2)$–$C(sp^3)$ 1·501 (7), and $C(sp^3)$–$C(sp^3)$ 1·516 (7) Å. The lengths of both C–O bonds are somewhat different, depending on the C atom hybridization: $C(sp^3)$–O 1·433 (6) and $C(sp^2)$–O 1·364 (6) Å. The geometries of the acetyl groups do not deviate from those of other structures reported in the literature.

References

CESARIO, M., GUILHEM, J. & MARTIN, J.-C. (1977). Fourth European Crystallographic Meeting, Oxford, pp. 458–460.

DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1, pp. 18–19. New York: Plenum.

GOULD, S. E. B., GOULD, R. O., REES, D. A. & WIGHT, A. W. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 392–398.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KRAJEWSKI, J. W., URBANCZYK-LIPKOWSKA, Z. & GLUZINSKI, P. (1979). *Acta Cryst.* B35, 519–522.

KRAJEWSKI, J. W., URBANCZYK-LIPKOWSKA, Z., GLUZINSKI, P., BLEIDELIS, J. & KEMME, A. (1978). *Acta Cryst.* A34, S 85.

LÓPEZ DE LERMA, J., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1973). *Acta Cryst.* B29, 537–541.

SCHWARTZ, J. C. P. (1973). *J. Chem. Soc. Chem. Commun.* pp. 505–508.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STOKHUYZEN, R. & CHUNG CHIEH (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 481–483.

N-Thiocinnamoylmorpholine

BY K. ANN KERR* AND PATRICK M. A. O. VAN ROEY

Departments of Chemistry and Physics, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

Abstract. $C_{13}H_{15}NOS$, monoclinic, $P2_1/c$, $a = 11·382$ (5), $b = 6·163$ (4), $c = 17·550$ (8) Å, $\beta = 102·16$ (3)°; $Z = 4$, $d_c = 1·288$ Mg m^{-3}. The planarity of the molecule together with the geometry of the thioamide fragment and the non-planar geometry of the N atom indicate competition between the N lone pair and the styrene moiety for the π orbital of the thiono group.

Introduction. The rotational barrier about the C–N bond of amides (Rogers & Woodbrey, 1962) and

thioamides (Sandström, 1962) is generally attributed to interaction between the lone-pair electrons on N and the π orbital of the thiono group. Such barriers can be measured by NMR spectroscopy through the coalescence temperatures of methyl or methylene protons of substituents on N. The introduction of groups capable of conjugation with the thiono group is reported to lower the barrier dramatically. For example, the activation energy for rotation in N,N-dimethyl-thioacetamide is 182·7 kJ mol^{-1} (Neuman & Young, 1965), but only 64·4 kJ mol^{-1} in N,N-dimethylthio-benzamide (Schwenker & Rosswag, 1967). A systematic study of the influence of conjugating

---