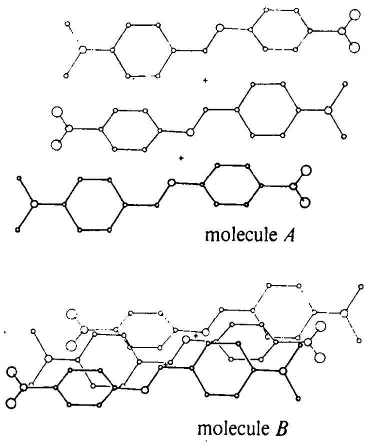

Fig. 6. Molecular stacking in the layer of molecule A and in the layer of molecule B for (II). The molecules are projected vertically on the plane of the central grouping atoms. The cross shows the position of an inversion centre.

one. The difference in the potential energies was estimated by them to be 1·5–2·0 kcal/mol for (VII), and about 3 kcal/mol for (VIII). It was suggested that the loss of the potential energy is compensated by the packing effect in each crystal. The packing effect on the molecular geometry is also found in the crystal of (II) in which the two independent molecules are twisted differently. The molecular shapes in different crystal fields will be determined in further investigations of the polymorphs of (II).

References

BERNSTEIN, J. (1972). *J. Chem. Soc. Perkin* II, pp. 946–950.

BERNSTEIN, J. (1975). *Acta Cryst.* **B31**, 1268–1271.

BERNSTEIN, J. & IZAK, I. (1975). *J. Cryst. Mol. Struct.* In the press.

BERNSTEIN, J. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin* II, pp. 951–955.

BEURSKENS, P. T. (1963). *Sign Correlation by the Sayre Equation.* Technical report, Univ. of Pittsburgh.

BREGMAN, J., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.

BÜRGI, H. B. & DUNITZ, J. D. (1970). *Helv. Chim. Acta*, **53**, 1747–1764.

BÜRGI, H. B. & DUNITZ, J. D. (1971). *Helv. Chim. Acta*, **54**, 1255–1260.

EZUMI, K., NAKAI, H., SAKATA, S., NISHIKIDA, K., SHIRO, M. & KUBOTA, T. (1974). *Chem. Lett.* pp. 1393–1398.

FINDER, C. J., NEWTON, M. G. & ALLINGER, N. L. (1974). *Acta Cryst.* **B30**, 411–415.

GRANT, D. F., KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* **B25**, 374–376.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Kynoch Press: Birmingham.

KOYANO, K. & TANAKA, I. (1965). *J. Phys. Chem.* **69**, 2545–2550.

KUBOTA, T., YAMAKAWA, M. & MORI, Y. (1963). *Bull. Chem. Soc. Japan*, **36**, 1552–1563; 1564–1572.

MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1970). *MULTAN, A System of Computer Programs for the Automatic Solution of Non-centrosymmetric Crystal Structures.* Univs. York, Louvain.

SKRABAL, P., STEIGER, J. & ZOLLINGER, H. (1975). *Helv. Chim. Acta*, **58**, 800–814.

Acta Cryst. (1976). **B32**, 1833

Stereochemistry of Unsaturated Amino Sugars. I. The Crystal and Molecular Structure of Peracetylated 2,3-Dideoxy-α-D-*threo*-aldopyranose

BY BISERKA KOJIĆ-PRODIĆ
'Ruđer Bošković' Institute, P.O. Box 1016, 41001 *Zagreb, Yugoslavia*
V. ROGIĆ
'Ruđer Bošković' Institute, P.O. Box 1016, 41001 *Zagreb, Yugoslavia, and Institute for Metallurgy,* 44000 *Sisak, Yugoslavia*
AND ŽIVA RUŽIĆ-TOROŠ
'Ruđer Bošković' Institute, P.O. Box 1016, 41001 *Zagreb, Yugoslavia*

(*Received* 12 *November* 1975; *accepted* 29 *December* 1975)

1,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose crystallizes in the space group $P2_12_12_1$ with $a=8\cdot332$, $b=13\cdot644$, $c=16\cdot345$ Å, $Z=4$. The structure was solved by direct methods and refined to an R of 0·038. The sugar ring appears in the $^0H_5$ half-chair conformation.

Introduction

A new class of unsaturated amino sugars has been synthesized and their infrared and NMR spectra studied (Pravdić & Fletcher, 1969; Pravdić, Židovec & Fletcher, 1970; Pravdić, Židovec & Fletcher, 1973; Pravdić, Židovec, Franjić & Fletcher, 1973).

The following acetylated 2-(*N*-acetylacetamido)-1,2-

(and -2,3-) unsaturated carbohydrates were submitted by Dr N. Pravdić for X-ray structure determination: 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose; 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranose; 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose; 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranose; 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose; 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose.

It has been suggested that 2,3-unsaturated sugars take part in metabolic pathways of ribonucleosides to deoxynucleosides (Lemieux, Fraga & Watanabe, 1968).

X-ray analysis of the above series is being carried out to provide information on molecular conformation, bond lengths and angles. Molecular shapes determined by this method refer to the molecules held rigidly in the crystal lattice and do not necessarily correspond to the conformation in solution. For the title compound the ${}^0H_5$ conformation was established by NMR spectra (Pravdić, Židovec & Fletcher, 1973) and is confirmed by this analysis.

Experimental

The space group was determined as $P2_12_12_1$ from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The intensities of 1813 observed reflexions [$I > 2\sigma(I)$] were measured on an automated Siemens AED four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation at the Instituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR. Crystal data are given in Table 1.

Table 1. *Crystallographic and physical data*

1,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose, $C_{16}H_{21}O_9N$

F.W.	371·35	Z	4
Space group	$P2_12_12_1$	D_m	1·324 g cm^{-3}
a	8·332 (4)* Å	D_c	1·329
b	13·644 (5)	μ(Cu $K\alpha$)	9·75 cm^{-1}
c	16·345 (6)	Crystal shape	Needle
U	1858·11 Å^3		

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.

The data were corrected for background, Lorentz and polarization effects, but not for absorption.

Structure determination and refinement

The overall temperature ($B = 3{\cdot}73$ Å^2) and scale factors were determined (Wilson, 1942) and used to compute normalized structure factors by routine *NORMAL* included in *MULTAN*. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). The solution was based on 300 reflexions with $|E| > 1{\cdot}3$. The E map corresponding to the solution with the best figure of merit revealed the positions of 23 non-hydrogen atoms. The remaining three atoms be-

Table 2. *Final atomic* (× 10⁴) *and thermal parameters* (Å² × 10³) *for non-hydrogen atoms*

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	257 (3)	1070 (2)	3146 (2)	32 (1)	32 (2)	42 (1)	1 (1)	−3 (1)	−1 (1)
C(2)	1216 (3)	954 (2)	3919 (2)	32 (1)	32 (2)	39 (1)	1 (1)	−2 (1)	−2 (1)
C(3)	2802 (3)	901 (2)	3917 (2)	33 (1)	36 (2)	39 (1)	2 (1)	−5 (1)	−3 (1)
C(4)	3745 (3)	1057 (2)	3149 (2)	29 (1)	27 (2)	45 (1)	0 (1)	−2 (1)	−6 (1)
C(5)	2682 (3)	1392 (2)	2454 (2)	32 (1)	32 (2)	40 (1)	−1 (1)	1 (1)	−1 (1)
C(6)	3438 (4)	1234 (3)	1624 (2)	40 (2)	55 (2)	45 (2)	4 (2)	7 (1)	−2 (1)
C(7)	−1584 (4)	2268 (3)	2628 (2)	40 (2)	67 (2)	61 (2)	14 (2)	1 (2)	21 (2)
C(8)	−1901 (6)	3341 (4)	2611 (3)	75 (3)	79 (3)	116 (4)	39 (3)	−5 (3)	25 (3)
C(9)	−479 (4)	−33 (3)	4783 (2)	38 (1)	52 (2)	52 (2)	2 (2)	−5 (1)	15 (2)
C(10)	−1700 (5)	−132 (3)	5453 (2)	57 (2)	74 (3)	66 (2)	−6 (2)	5 (2)	21 (2)
C(11)	349 (4)	1655 (3)	5245 (2)	44 (2)	69 (2)	46 (2)	0 (2)	4 (1)	−10 (2)
C(12)	1099 (6)	2586 (4)	4978 (3)	86 (3)	68 (3)	82 (2)	−21 (2)	30 (2)	−39 (2)
C(13)	5946 (3)	−48 (2)	3260 (2)	33 (1)	41 (2)	42 (1)	4 (1)	−2 (1)	1 (1)
C(14)	6707 (4)	−944 (3)	2916 (2)	52 (2)	54 (2)	68 (2)	19 (2)	−10 (2)	−19 (2)
C(15)	1601 (5)	1209 (3)	516 (2)	72 (2)	70 (3)	41 (2)	2 (2)	1 (2)	−10 (2)
C(16)	744 (8)	1843 (4)	−75 (3)	124 (5)	98 (4)	82 (3)	−2 (4)	−44 (3)	−2 (3)
O(0)	1173 (2)	876 (1)	2451 (1)	33 (1)	39 (1)	39 (1)	−1 (1)	−3 (1)	−3 (1)
O(1)	−317 (2)	2067 (2)	3134 (1)	38 (1)	43 (1)	50 (1)	12 (1)	−3 (1)	1 (1)
O(2)	−2286 (3)	1658 (2)	2255 (2)	61 (2)	91 (2)	94 (2)	−5 (2)	−38 (2)	21 (2)
O(3)	−155 (3)	−684 (2)	4322 (2)	58 (1)	43 (1)	78 (2)	−5 (1)	4 (1)	6 (1)
O(4)	−242 (4)	1573 (3)	5911 (1)	93 (2)	108 (2)	49 (1)	−15 (2)	22 (1)	−19 (1)
O(5)	4524 (2)	148 (1)	2902 (1)	31 (1)	35 (1)	54 (1)	5 (1)	−8 (1)	−10 (1)
O(6)	6510 (3)	451 (2)	3791 (1)	44 (1)	58 (1)	55 (1)	12 (1)	−14 (1)	−17 (1)
O(7)	2537 (3)	1753 (2)	1010 (1)	65 (1)	54 (1)	42 (1)	−4 (1)	−2 (1)	5 (1)
O(8)	1491 (4)	340 (2)	553 (2)	114 (2)	62 (2)	64 (1)	−4 (2)	−10 (2)	−19 (1)
N	292 (3)	886 (2)	4666 (1)	35 (1)	45 (1)	39 (1)	1 (1)	0 (1)	3 (1)

longing to the methyl groups were located from the subsequent Fourier synthesis.

Refinement was by full-matrix least-squares minimizing $\sum w||F_o|-|F_c||^2$ with $w=1/\sigma^2_{F_o}$. Heavy-atom coordinates, isotropic thermal parameters and a scale factor were refined to an R of 0·107. Two cycles of anisotropic refinement ($R=0·068$) and a difference synthesis were used to locate the H atoms. For three cycles the scale factor, the atomic coordinates for all atoms and the anisotropic thermal parameters for the heavy atoms (298 parameters in all) were varied. For H atoms, the isotropic thermal parameters are those of the bonded atom. The final agreement indices were

$$R=\sum ||F_o|-|F_c||/\sum |F_o|=0·038\ ,$$
$$R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}=0·049\ .$$

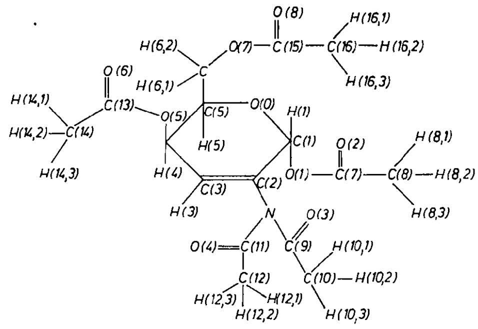

Fig. 1. Structural formula and numbering of the atoms.

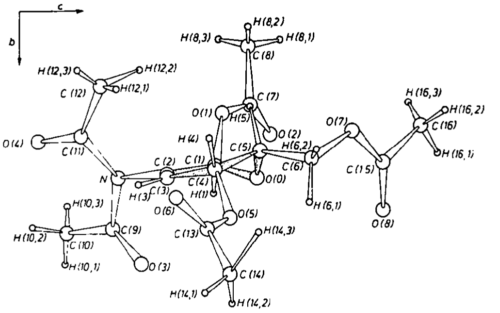

Fig. 2. Perspective view of the molecule showing ${}^{0}H_5$ conformation.

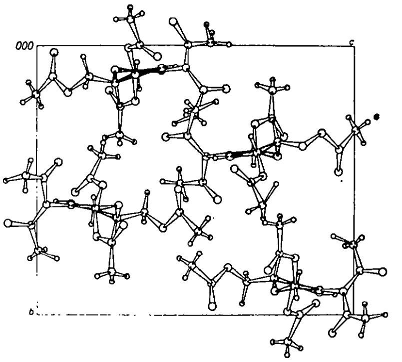

Fig. 3. A view of the crystal structure along **a**.

Scattering factors given by Cromer & Mann (1968) and, for H, by Stewart, Davidson & Simpson (1965) were used.

The calculations were carried out on the Univac 1110 computer at the University Computing Centre in Zagreb with the X-RAY 72/73 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972/1973). Atomic positional and thermal parameters are listed in Tables 2 and 3.*

Table 3. *Positional* (× 10^3) *and isotropic thermal parameters* (Å^2 × 10^2) *for hydrogen atoms*

	x	y	z	U
H(1)	−70 (4)	68 (2)	314 (2)	3·5
H(3)	340 (4)	74 (2)	439 (2)	3·2
H(4)	451 (4)	156 (2)	322 (2)	3·1
H(5)	247 (3)	214 (2)	259 (2)	3·3
H(6, 1)	346 (4)	52 (2)	150 (2)	4·2
H(6, 2)	452 (4)	149 (2)	162 (2)	4·2
H(8, 1)	−243 (6)	343 (3)	209 (3)	8·1
H(8, 2)	−102 (5)	365 (3)	257 (2)	8·1
H(8, 3)	−245 (6)	355 (3)	300 (2)	8·1
H(10, 1)	−196 (5)	−78 (3)	526 (2)	6·1
H(10, 2)	−129 (4)	−5 (3)	602 (2)	6·1
H(10, 3)	−253 (5)	40 (2)	545 (2)	6·1
H(12, 1)	200 (5)	257 (3)	478 (2)	6·5
H(12, 2)	68 (5)	289 (3)	442 (2)	6·5
H(12, 3)	104 (5)	296 (3)	530 (2)	6·5
H(14, 1)	770 (4)	−120 (2)	332 (2)	5·1
H(14, 2)	604 (4)	−142 (2)	286 (2)	5·1
H(14, 3)	707 (4)	−75 (3)	247 (2)	5·1
H(16, 1)	1 (5)	148 (3)	−34 (3)	8·7
H(16, 2)	152 (6)	226 (3)	−39 (3)	8·7
H(16, 3)	10 (6)	231 (3)	18 (3)	8·7

Description and discussion of the structure

The structural formula and numbering of the atoms are given in Fig. 1. A perspective view of the molecule is shown in Fig. 2. Molecular packing is illustrated in Fig. 3.

Table 4. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·503 (4)	C(1)—H(1)	0·96 (3)
C(2)—C(3)	1·323 (4)	C(3)—H(3)	0·94 (3)
C(3)—C(4)	1·495 (4)	C(4)—H(4)	0·94 (3)
C(4)—C(5)	1·511 (4)	C(5)—H(5)	1·06 (3)
C(5)—O(0)	1·440 (3)	C(6)—H(6, 1)	1·00 (3)
C(1)—O(0)	1·394 (3)	C(6)—H(6, 2)	0·96 (3)
C(1)—O(1)	1·443 (4)	C(8)—H(8, 1)	0·97 (4)
C(4)—O(5)	1·457 (3)	C(8)—H(8, 2)	0·85 (4)
C(6)—O(7)	1·440 (4)	C(8)—H(8, 3)	0·84 (4)
C(5)—C(6)	1·510 (4)	C(10)-H(10, 1)	0·96 (4)
C(2)—N	1·448 (4)	C(10)-H(10, 2)	0·99 (3)
C(9)—N	1·421 (4)	C(10)-H(10, 3)	1·00 (4)
C(11)-N	1·414 (4)	C(12)-H(12, 1)	0·82 (4)
C(7)—O(1)	1·369 (4)	C(12)-H(12, 2)	1·06 (4)
C(13)-O(5)	1·348 (3)	C(12)-H(12, 3)	0·73 (4)
C(15)-O(7)	1·346 (5)	C(14)-H(14, 1)	1·12 (3)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31579 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4 (*cont.*)

C(7)—O(2)	1·186 (5)	C(14)-H(14,2)	0·86 (3)
C(9)—O(3)	1·196 (4)	C(14)-H(14,3)	0·83 (3)
C(11)-O(4)	1·199 (4)	C(16)-H(16,1)	0·90 (4)
C(13)-O(6)	1·199 (4)	C(16)-H(16,2)	1·00 (5)
C(15)-O(8)	1·190 (5)	C(16)-H(16,3)	0·93 (5)
C(7)—C(8)	1·488 (6)		
C(9)—C(10)	1·500 (5)		
C(11)-C(12)	1·483 (6)		
C(13)-C(14)	1·488 (5)		
C(15)-C(16)	1·481 (7)		

Pyranose ring

O(0)-C(1)-C(2)	112·0 (2)	C(2)-C(3)-H(3)	122 (2)
C(1)-C(2)-C(3)	122·3 (2)	H(3)-C(3)-C(4)	116 (2)
C(2)-C(3)-C(4)	121·2 (2)	C(3)-C(4)-H(4)	111 (2)
C(3)-C(4)-C(5)	111·5 (2)	H(4)-C(4)-O(5)	111 (2)
C(4)-C(5)-O(0)	111·5 (2)	C(3)-C(4)-O(5)	110·2 (2)
C(5)-O(0)-C(1)	112·5 (2)	H(4)-C(4)-C(5)	106 (2)
O(0)-C(1)-H(1)	110 (2)	O(5)-C(4)-C(5)	108·1 (2)
C(2)-C(1)-H(1)	113 (2)	C(4)-C(5)-H(5)	103 (1)
O(0)-C(1)-O(1)	110·5 (2)	C(4)-C(5)-C(6)	112·8 (2)
H(1)-C(1)-O(1)	104 (2)	C(6)-C(5)-O(0)	106·9 (2)
O(1)-C(1)-C(2)	106·6 (2)	C(6)-C(5)-H(5)	113 (1)
C(1)-C(2)-N	115·7 (2)	H(5)-C(5)-O(0)	109 (2)
N——C(2)-C(3)	122·0 (2)		

C(6)-O(7)-Acetyl group

C(5)——C(6)—O(7)	109·8 (3)
C(5)——C(6)—H(6,1)	109 (2)
C(5)——C(6)—H(6,2)	110 (2)
H(6,1)—C(6)—H(6,2)	109 (3)
H(6,1)—C(6)—O(7)	111 (2)
H(6,2)—C(6)—O(7)	108 (2)
C(6)——O(7)—C(15)	116·7 (3)
O(7)——C(15)-O(8)	124·3 (3)
O(7)——C(15)-C(16)	110·4 (4)
O(8)——C(15)-C(16)	125·2 (4)
C(15)——C(16)-H(16,1)	109 (3)
C(15)——C(16)-H(16,2)	111 (3)
C(15)——C(16)-H(16,3)	113 (3)
H(16,1)-C(16)-H(16,2)	120 (4)
H(16,1)-C(16)-H(16,3)	102 (4)
H(16,2)-C(16)-H(16,3)	102 (4)

Interatomic distances and angles are listed in Table 4, and displacements of the atoms from the least-squares plane through the sugar ring in Table 5. Dihedral angles defining the conformation are presented in Table 6.

Table 5. *Least-squares plane through the sugar ring*

Atoms included in the calculation of the plane are denoted by an asterisk.

	Displacement (Å)
C(1)*	−0·012
C(2)*	0·027
C(3)*	−0·027
C(4)*	0·012
C(5)	0·287
O(0)	−0·427
N	0·100
H(3)	−0·123

The sugar ring exhibits a half-chair ${}^0H_5$ conformation (Fig. 2). The best least-squares plane is defined by C(1), C(2), C(3) and C(4); C(5) and O(0) are displaced from this plane by 0·287 and −0·427 Å respectively. Due to the presence of the double bond C(2)=C(3), the N and H(3) atoms should be coplanar with C(1), C(2), C(3) and C(4). The N atom is displaced by 0·100 and H(3) by 0·123 Å.

Puckering of the sugar ring is described by dihedral angles C(3)-C(4)-C(5)-O(0) of −40·5 (3)°, C(4)-C(5)-O(0)-C(1) of 64·1 (3)° and C(5)-O(0)-C(1)-C(2) of −49·3 (3)° (Table 6). Sundaralingam (1968) has defined the conformation about C(5)-C(6) in pyranosides by the angle φ_{OO} = O(5)-C(5)-C(6)-O(6). In the present compound this angle is described by the sequence O(0)-C(5)-C(6)-O(7) and its value of 69·5 (3)° is in

Table 4 (*cont.*)

O(1)-Acetyl group

C(1)——O(1)—C(7)	116·9 (2)
O(1)——C(7)—O(2)	123·4 (3)
O(1)——C(7)—C(8)	110·2 (3)
O(2)——C(7)—C(8)	126·4 (4)
C(7)——C(8)—H(8,1)	103 (3)
C(7)——C(8)—H(8,2)	109 (3)
C(7)——C(8)—H(8,3)	115 (3)
H(8,1)—C(8)—H(8,2)	106 (4)
H(8,1)—C(8)—H(8,3)	112 (4)
H(8,2)—C(8)—H(8,3)	111 (4)

O(5)-Acetyl group

C(4)——O(5)—C(13)	116·1 (2)
O(5)——C(13)-O(6)	123·1 (3)
O(5)——C(13)-C(14)	111·9 (3)
O(6)——C(13)-C(14)	125·0 (3)
C(13)——C(14)-H(14,1)	111 (2)
C(13)——C(14)-H(14,2)	113 (2)
C(13)——C(14)-H(14,3)	103 (2)
H(14,1)-C(14)-H(14,2)	108 (3)
H(14,1)-C(14)-H(14,3)	110 (3)
H(14,2)-C(14)-H(14,3)	113 (3)

N-Acetyl groups

C(2)——N——C(9)	114·3 (2)
N———C(9)—O(3)	117·9 (3)
O(3)——C(9)—C(10)	123·1 (3)
N———C(9)—C(10)	118·9 (3)
C(9)——C(10)-H(10,1)	90 (2)
C(9)——C(10)-H(10,2)	116 (2)
C(9)——C(10)-H(10,3)	114 (2)
H(10,1)-C(10)-H(10,2)	119 (3)
H(10,1)-C(10)-H(10,3)	121 (3)
H(10,2)-C(10)-H(10,3)	99 (3)
C(2)——N——C(11)	119·9 (3)
N———C(11)-O(4)	121·6 (3)
N———C(11)-C(12)	116·9 (3)
C(11)——N——C(9)	125·4 (3)
O(4)——C(11)-C(12)	121·4 (4)
C(11)——C(12)-H(12,1)	118 (3)
C(11)——C(12)-H(12,2)	116 (2)
C(11)——C(12)-H(12,3)	110 (3)
H(12,1)-C(12)-H(12,2)	88 (3)
H(12,1)-C(12)-H(12,3)	112 (4)
H(12,2)-C(12)-H(12,3)	110 (4)

Table 6. *Dihedral angles* (°)

In pyranose ring	
O(0)–C(1)–C(2)–C(3)	14·4 (4)
C(1)–C(2)–C(3)–C(4)	6·4 (5)
C(2)–C(3)–C(4)–C(5)	7·1 (4)
C(3)–C(4)–C(5)–O(0)	−40·5 (3)
C(4)–C(5)–O(0)–C(1)	64·1 (3)
C(5)–O(0)–C(1)–C(2)	−49·3 (3)
On pyranose ring	
O(0)–C(1)–C(2)–N	−164·4 (2)
C(1)–C(2)–C(3)–H(3)	−171 (2)
C(2)–C(3)–C(4)–H(4)	124 (2)
C(2)–C(3)–C(4)–O(5)	−113·0 (3)
C(3)–C(4)–C(5)–H(5)	77 (2)
C(3)–C(4)–C(5)–C(6)	−160·8 (3)
C(5)–O(0)–C(1)–H(1)	−176 (2)
C(5)–O(0)–C(1)–O(1)	69·4 (3)
O(0)–C(5)–C(4)–H(4)	−161 (2)
O(0)–C(5)–C(4)–O(5)	80·8 (3)
H(5)–C(5)–O(0)–C(1)	−49 (2)
C(6)–C(5)–O(0)–C(1)	−172·1 (2)
C(3)–C(2)–C(1)–H(1)	139 (2)
C(3)–C(2)–C(1)–O(1)	−106·5 (3)
H(1)–C(1)–C(2)–N	−40 (2)
O(1)–C(1)–C(2)–N	74·7 (3)
N—C(2)–C(3)–H(3)	7 (2)
H(3)–C(3)–C(4)–H(4)	−58 (3)
H(3)–C(3)–C(4)–O(5)	65 (2)
H(4)–C(4)–C(5)–H(5)	−44 (2)
H(4)–C(4)–C(5)–C(6)	79 (2)
O(5)–C(4)–C(5)–H(5)	−162 (2)
O(5)–C(4)–C(5)–C(6)	−39·5 (3)
Acetyl groups	
H(1)—C(1)—O(1)—C(7)	−41 (2)
C(1)—O(1)—C(7)—O(2)	5·7 (5)
C(1)—O(1)—C(7)—C(8)	−173·3 (3)
C(2)—N—C(9)—O(3)	8·5 (4)
C(2)—N—C(9)—C(10)	−169·2 (3)
C(2)—N—C(11)–O(4)	−170·9 (3)
C(2)—N—C(11)–C(12)	12·2 (4)
C(10)—C(9)—N—C(11)	17·8 (5)
O(3)—C(9)—N—C(11)	−164·6 (3)
C(12)—C(11)–N—C(9)	−175·1 (3)
O(4)—C(11)–N—C(9)	1·8 (5)
H(4)—C(4)—O(5)—C(13)	38 (2)
C(4)—O(5)—C(13)–O(6)	4·9 (4)
C(4)—O(5)—C(13)–C(14)	−175·1 (2)
H(5)—C(5)—C(6)—O(7)	−51 (2)
C(5)—C(6)—O(7)—C(15)	−105·4 (3)
C(6)—O(7)—C(15)–O(8)	−0·8 (5)
C(6)—O(7)—C(15)–C(16)	179·5 (3)
H(6,1)–C(6)—O(7)—C(15)	15 (2)
H(6,2)–C(6)—O(7)—C(15)	135 (2)
Others	
O(0)–C(1)–O(1)–C(7)	76·8 (3)
C(2)–C(1)–O(1)–C(7)	−161·3 (2)
C(1)–C(2)–N—C(9)	75·0 (3)
C(1)–C(2)–N—C(11)	−111·5 (3)
C(3)–C(2)–N—C(9)	−103·9 (3)
C(3)–C(2)–N—C(11)	69·6 (4)
C(3)–C(4)–O(5)–C(13)	−84·3 (3)
C(5)–C(4)–O(5)–C(13)	153·6 (2)
C(4)–C(5)–C(6)–O(7)	−167·6 (2)
O(0)–C(5)–C(6)–O(7)	69·5 (3)
C(4)–C(5)–C(6)–H(6,1)	71 (2)
C(4)–C(5)–C(6)–H(6,2)	−49 (2)
O(0)–C(5)–C(6)–H(6,1)	−52 (2)
O(0)–C(5)–C(6)–H(6,2)	−172 (2)
H(5)–C(5)–C(6)–H(6,1)	−173 (3)
H(5)–C(5)–C(6)–H(6,2)	68 (3)

the range +60° ± 30° common for pyranoside derivatives.

The ring substituents are attached at C(1) in quasi-equatorial, C(4) in quasi-axial and C(5) in equatorial positions (Fig. 2) (Stoddart, 1971). The conformation found is in agreement with NMR data (Pravdić, Židovec & Fletcher, 1973).

The mean value of the C–C length in the ring is 1·507 (4) Å. The shortening of C(3)–C(4) to 1·495 (4) Å can be explained by the presence of the C(2)=C(3) double bond. In the acetyl groups the mean C–C length of 1·488 (7) Å is reasonable for a single bond next to a C=O bond. There are two categories of C–O bonds: the C–O bonds range from 1·440 (3) to 1·457 (3) Å and the O–C=O bonds from 1·346 (5) to 1·369 (4) Å. The anomeric C(1)–O(1) length of 1·443 (3) Å does not deviate significantly from other C–O bond distances in the molecule. Endocyclic bonds C(1)–O(0) [1·394 (3)] and C(5)–O(0) [1·440 (3) Å] are asymmetric with well-pronounced differences from the normal C–O single-bond distance of 1·428 Å (Sundaralingam, 1968). The carbonyl bonds are in the range 1·186 (5) to 1·199 (4) Å.

The endocyclic valence angles at C(1), C(4) and C(5) range from 111·5 (2)° to 112·5 (2)° and are slightly greater than the tetrahedral angle of 109·5°. These values can be compared with those found in other pyranose derivatives (Kim & Jeffrey, 1967; Sundaralingam, 1968). The value of the angle O(0)–C(1)–O(1) of 110·5 (2)° is a little greater than the tetrahedral value. The intermolecular O(1)···O(0) distance for this α-anomer is 2·330 (3) Å. The valence angle of the ring O atom is 112·5 (2)°, close to the value of 112·9 (4)° found in *N*-acetyl-α-D-galactosamine (Gilardi & Flippen, 1974). The C valence angles exterior to the pyranose ring show a wider range [106·0 (2)° to 112·8 (2)°] than the interior angles.

All the hydroxyl groups are acetylated, and O–H···O hydrogen bonds are not possible. From the intermolecular distances and angles there is no evidence for C–H···O hydrogen bonds.

The authors are grateful to Professor M. Nardelli for facilities placed at their disposal. We thank Drs A. Mangia and G. Pelizzi for collecting the intensities, and Dr N. Pravdić for growing the crystals and for many helpful discussions.

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Declercq, J. P., Germain, G., Main, P. & Woolfson, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

Gilardi, D. R. & Flippen, J. L. (1974). *Acta Cryst.* B**30**, 2931–2933.

Kim, S. H. & Jeffrey, G. A. (1967). *Acta Cryst.* **22**, 537–545.

LEMIEUX, R. U., FRAGA, E. & WATANABE, K. A. (1968). *Canad. J. Chem.* **46**, 61–69.
PRAVDIĆ, N. & FLETCHER, H. G. JR (1969). *Croat. Chem. Acta*, **41**, 125–133.
PRAVDIĆ, N., ŽIDOVEC, B. & FLETCHER, H. G. JR (1970). *Croat. Chem. Acta*, **32**, 523–533.
PRAVDIĆ, N., ŽIDOVEC, B. & FLETCHER, H. G. JR (1973). *Croat. Chem. Acta*, **45**, 333–342.
PRAVDIĆ, N., ŽIDOVEC, B., FRANJIĆ, I. & FLETCHER, H. G. JR (1973). *Croat. Chem. Acta*, **45**, 343–356.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972/1973). X-RAY 72/73 system. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
STODDART, J. F. (1971). *Stereochemistry of Carbohydrates*, pp. 50–60. New York: John Wiley.
SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1976). B**32**, 1838

Dioxygen Tetra(dimethylphenylphosphine)iridium(I) Tetraphenylborate

BY MAGRIET NOLTE AND ERIC SINGLETON

National Chemical Research Laboratory, CSIR, P.O. Box 395, Pretoria, Republic of South Africa

(*Received* 24 *November* 1975; *accepted* 22 *December* 1975)

$[IrO_2\{PC_6H_5(CH_3)_2\}_4]B(C_6H_5)_4$, triclinic, $P\bar{1}$, $a=17{\cdot}62$ (2), $b=14{\cdot}30$ (2), $c=11{\cdot}46$ (2) Å, $\alpha=104{\cdot}85$ (5), $\beta=105{\cdot}20$ (5), $\gamma=93{\cdot}18$ (5)°, $Z=2$, $D_c=1{\cdot}37$ g cm^{-3}, $M=1096$. O–O = 1·49; Ir–O = 2·04, 2·05; Ir–P(ax) = 2·39, 2·40; Ir–P(eq) = 2·31, 2·33 Å. The compound is isostructural with the Rh analogue.

Introduction

The cations $[RhO_2L_4]^+$ [$L=As(CH_3)_2(C_6H_5)$, $P(CH_3)_2(C_6H_5)$] (Nolte & Singleton, 1975, 1976) have similar O–O bond lengths of 1·46 and 1·43 Å respectively, in line with the comparable donor properties of $As(CH_3)_2(C_6H_5)$ and $P(CH_3)_2(C_6H_5)$. The close similarity to the length of 1·42 Å found for O–O in $[RhO_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$ (McGinnety, Payne & Ibers, 1969) does not fit the trends previously postulated, relating ligand basicity with O–O length in other Rh and Ir dioxygen complexes (McGinnety, Doedens & Ibers, 1967). As a further test of the effects of a change of both metal and ligand on M–O and O–O parameters, the structure of the salt $[IrO_2\{P(CH_3)_2(C_6H_5)\}_4]B(C_6H_5)_4$ was undertaken. If ligand effects are more enhanced in Ir than in Rh compounds, then changing from $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ to the more basic $\{P(CH_3)_2(C_6H_5)\}_2$ would be expected to cause a further elongation of the O–O bond, and this effect should also be coupled with a shortening of the Ir–O bonds if Chatt–Dewar type bonding (Chatt & Duncanson, 1953; Dewar, 1951) is operating.

A prismatic crystal, 0·16 × 0·20 × 0·44 mm, was used for data collection. Intensities were collected on a Philips PW1100 four-circle diffractometer over the range $\theta=3$–18° with graphite-monochromated Mo $K\alpha$ radiation. The ω–2θ scan mode was used. Of the 3662 reflexions recorded, 3312 had $I>2\sigma(I)$ and were considered observed. Three standard reflexions were remeasured every hour. They decreased by 8, 5 and 4% during the 68 hour period of data collection; no correction was made for crystal decomposition. Background, Lp and absorption corrections were applied; transmission coefficients varied from 0·51 to 0·74 ($\mu=28{\cdot}2$ cm^{-1}). No corrections were made for extinction. Although the compound appeared to be isostructural with the Rh analogue (Nolte & Singleton, 1976) the structure was solved independently by Patterson and Fourier methods. Least-squares refinement was carried out by the full-matrix technique alternately for different sets of non-hydrogen atoms. Calculations were performed with the *CRYLSQ* program of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on an IBM 360/65 computer.

All atoms were refined anisotropically with a weighting scheme to reduce the effect of reflexions with large F(obs) and/or small θ values. The final R was 0·054 for the observed intensities. The scattering factors were those of Cromer & Mann (1968), corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1.* Bond lengths and angles (calculated by the program *BONDLA*, not corrected for thermal motion) are summarized in Tables 2 and 3. Atomic numbering is given in Fig. 1 and a stereo view in Fig. 2, drawn by the program *ORTEP* (Johnson, 1965).

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31576 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.