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Diheterolevulosan IV: Di-β-D-fructopyranose 1,2′:2,1′-Dianhydride

By Jan A. Kanters, Arie Schouten and Jan Kroon

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, 3584 *CH Utrecht, The Netherlands*

Mohamed Mathlouthi

Faculté des Sciences, Chimie Physique Industrielle, Université de Reims Champagne Ardenne, BP 347 – *Moulin de la Housse, F*-51062 *Reims CEDEX, France*

and Joop H. van der Maas and Bert Lutz

Laboratory for Analytical Chemistry, Rijksuniversiteit Utrecht, Croesestraat 77*a*, 3522 *AD Utrecht, The Netherlands*

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Abstract. $C_{12}H_{20}O_{10}$, $M_r = 324{\cdot}29$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}8462\ (3)$, $b = 7{\cdot}3826\ (4)$, $c = 26{\cdot}106\ (2)$ Å, $V = 1319{\cdot}47$ Å^3, $Z = 4$, $D_x = 1{\cdot}632$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54184$ Å, $\mu = 12{\cdot}0$ cm^{-1}, $F(000) = 688$, $T = 295$ K, final $R = 0{\cdot}030$ for 1468 reflections with $I \geq 2{\cdot}5\sigma(I)$. The molecule consists of two similar β-D-fructopyranose fragments which are connected by a dioxane ring. The fructose rings have $^2C_5\ (1C)$ chair conformations, the dioxane ring has a distorted boat conformation with the O atoms at the bows. All hydroxyl groups act as donors in intermolecular hydrogen bonds. Each molecule is hydrogen-bonded to six surrounding molecules by 14 hydrogen bonds, thus forming a closely knit three-dimensional network. There are three bifurcated planar hydrogen-bond configurations present in the structure. Two hydrogen bonds have large O···O separations [3·142 (3) and 3·160 (2) Å] and one is very short [2·623 (2) Å]. This distance variation gives rise to unusual IR absorptions in the OH-stretch region.

Introduction. On treatment with anhydrous hydrogen fluoride, inuline and D-fructose are quantitatively converted into a mixture of D-fructose dianhydrides which differ in ring size, *i.e.* pyranose or furanose rings, and/or in anomeric configurations (Defaye, Gadelle & Pedersen, 1985). Furthermore, non-anomeric C atoms may be involved in the formation of the interglycosidic dioxane ring which leads to the possible formation of a relatively large number of isomers. However, it was pointed out (Bock, Pedersen, Defaye & Gadelle, 1985; Defaye, Gadelle & Pedersen, 1987) that the course of anhydride formation is mainly controlled by anomeric and *exo*-anomeric effects, which is at the origin of the low number of stable, isolated isomers. Five of these 1,2′:2,1′-dianhydrides have been isolated from reaction mixtures of inuline and anhydrous hydrogen fluoride and the structures of these compounds have been assigned by ^{13}C NMR spectroscopy (Binkley, Binkley & Grey, 1973; Binkley, Binkley & Wickberg, 1974; Defaye *et al.*, 1985).

If α- or β-D-fructopyranose is dentoed by α- or β-D-Fp and α- or β-D-fructofuranose by α- or β-D-Ff these 1,2′:2,1′-dianhydrides are, in abbreviated form, α-D-Fp-β-D-Fp (diheterolevulosan I), α-D-Ff-β-D-Fp (diheterolevulsan II), β-D-Ff-β-D-Fp (diheterolevulosan III), β-D-Fp-β-D-Fp (diheterolevulosan IV) and α-D-Ff-β-D-Ff (the so-called difructose dianhydride I, Irvine & Stevenson, 1929; McDonald & Jackson, 1940).

The fructose dianhydrides are non-reducing saccharide derivatives and therefore do not undergo transformations in solution. Because of this property and the molecular rigidity imposed by the central dioxane ring, these compounds constitute ideal models for the study of the relation between structure and sweet taste.

So far only the X-ray analysis of diheterolevulsan I has been mentioned in the literature (Defaye *et al.*, 1985), but no structural details were given. Here we report the crystal structure of diheterolevulsan IV.

Experimental. A colourless crystal with dimensions 0·7 × 0·4 × 0·3 mm was used for the data collection. Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation. Lattice parameters were determined by least-squares fitting of the angular settings of 20 reflections in the θ range 13·13–20·06°. The ω–2θ scan mode was applied with $\Delta\omega = (0{\cdot}55 + 0{\cdot}35\tan\theta)°$. Intensities of 1483 unique reflections were

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collected with $2\theta_{\max} = 140°$ and $0 \le h \le 8$, $0 \le k \le 8$ and $0 \le l \le 31$ of which 1468 reflections were above the $2{\cdot}5\sigma(I)$ level. Two periodically measured standard reflections (339 and $\overline{339}$) showed an r.m.s. deviation of 0·7%. Lp corrections, no correction for absorption.

The structure was solved by direct methods (*SHELX*86, Sheldrick, 1986). The H atoms were located on difference Fourier maps and included in the refinement with an overall isotropic thermal parameter, which refined to 0·030 Å^2. Anisotropic full-matrix least-squares refinement on F of 260 parameters (scale factor, atomic coordinates, anisotropic thermal parameters of non-H atoms and a general isotropic thermal parameter for H atoms) converged at $R = 0{\cdot}030$ and $wR = 0{\cdot}038$ with $w = \sigma(F_o)^{-2}$, goodness-of-fit $S = 0{\cdot}45$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}0009$, $(\Delta/\sigma)_{\max} = 0{\cdot}005$. Maximum and minimmum residual density in the final difference map 0·18 and $-0{\cdot}21$ e Å^{-3} respectively. Calculations were performed with *SHELX*76 (Sheldrick, 1976) (refinement) and the *EUCLID* package (Spek, 1982) (geometry and illustrations) on a MicroVAXII computer.

Scattering factors for non-H atoms were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965) and anomalous-dispersion terms from Cromer & Liberman (1970).

The IR spectrum was recorded following the KBr disc technique on a PE 1800 Ft-IR spectrometer (resolution 2 cm^{-1}, 400 scans).

Discussion. The atomic parameters are given in Table 1.* A perspective view of the molecule with atomic numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. A view of the crystal structure together with the hydrogen bonds is displayed in Fig. 2.

The D-fructose rings have a $^2C_5$ (1C) chair conformation, which has also been observed in the structure of β-D-fructose (Kanters, Roelofsen, Alblas & Meinders, 1977). The link between the fructose rings is a dispirodioxane ring which adopts a distorted boat conformation with both O atoms at the bows. The θ and φ puckering parameters of Cremer & Pople (1975) of the fructose rings are 171·6 (2), 252 (2) and 176·5 (2), 97 (3)° respectively. For the dioxane ring these values are 87·6 (2) and 8·6 (2)°, the angle between the two C—O—C planes is 78·9 (2)° and the angles between the C(1)—C(2) and C(11)—C(12) bonds is 8·0 (2)°.

Table 1. *Final coordinates and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$ (Å^2)
O(1)	0·8481 (2)	0·8712 (2)	0·08444 (5)	0·0207 (4)
O(2)	0·9165 (2)	0·5817 (2)	0·13458 (5)	0·0207 (4)
O(3)	0·5230 (3)	0·5299 (3)	0·10238 (5)	0·0287 (5)
O(4)	0·4424 (3)	0·2788 (3)	0·17847 (7)	0·0376 (6)
O(5)	0·5212 (3)	0·4687 (3)	0·26584 (6)	0·0365 (5)
O(6)	0·7994 (2)	0·7127 (2)	0·21037 (5)	0·0234 (4)
O(13)	1·0964 (3)	0·7064 (2)	0·01462 (6)	0·0291 (5)
O(14)	1·2727 (3)	1·0282 (2)	−0·02799 (5)	0·0271 (5)
O(15)	1·4207 (3)	1·1603 (3)	0·06303 (7)	0·0339 (5)
O(16)	1·1147 (2)	1·0056 (2)	0·12547 (5)	0·0244 (4)
C(1)	0·7356 (3)	0·8626 (3)	0·13080 (8)	0·0233 (6)
C(2)	0·7619 (3)	0·6780 (3)	0·15733 (8)	0·0196 (5)
C(3)	0·5822 (3)	0·5562 (3)	0·15352 (7)	0·0202 (6)
C(4)	0·6200 (3)	0·3771 (3)	0·18050 (8)	0·0244 (6)
C(5)	0·6834 (4)	0·4093 (3)	0·23575 (8)	0·0267 (6)
C(6)	0·8439 (4)	0·5501 (3)	0·23883 (8)	0·0272 (6)
C(11)	1·0883 (3)	0·6878 (3)	0·12871 (9)	0·0233 (6)
C(12)	1·0515 (3)	0·8571 (3)	0·09571 (7)	0·0188 (6)
C(13)	1·1662 (3)	0·8530 (3)	0·04531 (8)	0·0200 (6)
C(14)	1·1566 (3)	1·0331 (3)	0·01723 (7)	0·0217 (6)
C(15)	1·2192 (4)	1·1857 (3)	0·05242 (9)	0·0258 (6)
C(16)	1·0945 (4)	1·1781 (3)	0·10044 (9)	0·0276 (7)

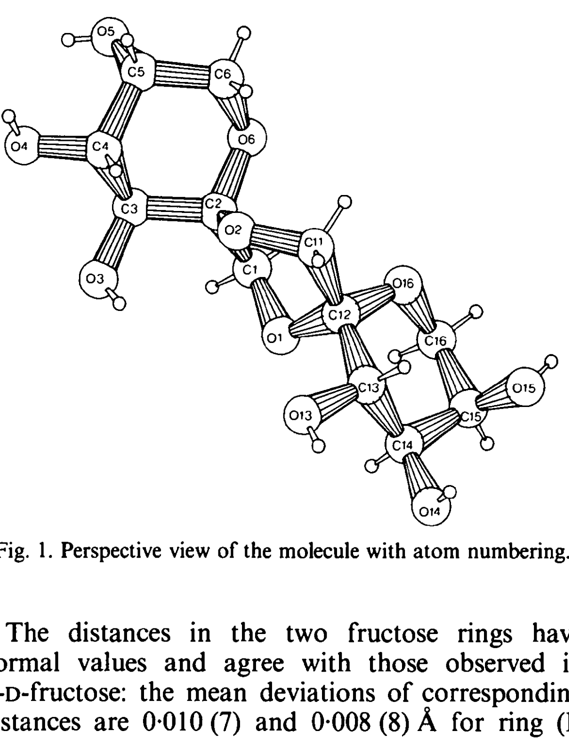

Fig. 1. Perspective view of the molecule with atom numbering.

The distances in the two fructose rings have normal values and agree with those observed in β-D-fructose: the mean deviations of corresponding distances are 0·010 (7) and 0·008 (8) Å for ring (I) and ring (II) respectively. The same holds for the bond angles with mean deviations of 1·4 (10) and 1·8 (11)° respectively. The anomeric effect, *i.e.* the shortening of the exocyclic C(2)—O(2) bond and the discrepancy between the endocyclic C(2)—O(6) and C(6)—O(6) bonds, which is present in β-D-fructose, is much less pronounced in the dianhydride. In ring (I) these distances are 1·407 (3), 1·431 (2) and 1·444 (3) Å, in ring (II) 1·427 (2), 1·412 (3) and 1·438 (3) Å respectively.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52114 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°)

O(1)—C(1)	1·436 (2)	O(6)—C(6)	1·444 (3)	C(3)—C(4)	1·520 (3)
O(1)—C(12)	1·427 (2)	O(13)—C(13)	1·429 (3)	C(4)—C(5)	1·525 (3)
O(2)—C(2)	1·407 (3)	O(14)—C(14)	1·424 (2)	C(5)—C(6)	1·515 (4)
O(2)—C(11)	1·421 (3)	O(15)—C(15)	1·419 (3)	C(11)—C(12)	1·539 (3)
O(3)—C(3)	1·409 (2)	O(16)—C(12)	1·412 (3)	C(12)—C(13)	1·533 (3)
O(4)—C(4)	1·417 (3)	O(16)—C(16)	1·438 (3)	C(13)—C(14)	1·520 (3)
O(5)—C(5)	1·429 (3)	C(1)—C(2)	1·539 (3)	C(14)—C(15)	1·516 (3)
O(6)—C(2)	1·431 (2)	C(2)—C(3)	1·527 (3)	C(15)—C(16)	1·518 (3)

C(1)—O(1)—C(12)	110·3 (1)	C(4)—C(5)—C(6)	111·3 (2)
C(2)—O(6)—C(6)	112·8 (2)	O(6)—C(6)—C(5)	113·0 (2)
C(2)—O(2)—C(11)	112·9 (2)	O(2)—C(11)—C(12)	111·9 (2)
C(12)—O(16)—C(16)	114·1 (2)	O(1)—C(12)—O(16)	110·8 (2)
O(1)—C(1)—C(2)	110·8 (2)	O(1)—C(12)—C(11)	109·5 (2)
O(2)—C(2)—O(6)	111·3 (2)	O(1)—C(12)—C(13)	108·9 (2)
O(2)—C(2)—C(1)	110·2 (2)	O(16)—C(12)—C(11)	105·8 (2)
O(2)—C(2)—C(3)	106·3 (2)	O(16)—C(12)—C(13)	109·3 (2)
O(6)—C(2)—C(1)	107·3 (2)	C(11)—C(12)—C(13)	112·4 (2)
O(6)—C(2)—C(3)	108·2 (2)	O(13)—C(13)—C(12)	109·0 (2)
C(1)—C(2)—C(3)	113·4 (2)	O(13)—C(13)—C(14)	112·2 (2)
O(3)—C(3)—C(2)	112·0 (2)	C(12)—C(13)—C(14)	112·0 (2)
O(3)—C(3)—C(4)	111·6 (2)	O(14)—C(14)—C(13)	110·7 (2)
C(2)—C(3)—C(4)	110·2 (2)	O(14)—C(14)—C(15)	111·3 (2)
O(4)—C(4)—C(3)	106·4 (2)	C(13)—C(14)—C(15)	110·2 (2)
O(4)—C(4)—C(5)	111·1 (2)	O(15)—C(15)—C(14)	107·2 (2)
C(3)—C(4)—C(5)	110·6 (2)	O(15)—C(15)—C(16)	112·4 (2)
O(5)—C(5)—C(4)	110·3 (2)	C(14)—C(15)—C(16)	108·3 (2)
O(5)—C(5)—C(6)	108·9 (2)	O(16)—C(16)—C(15)	110·7 (2)

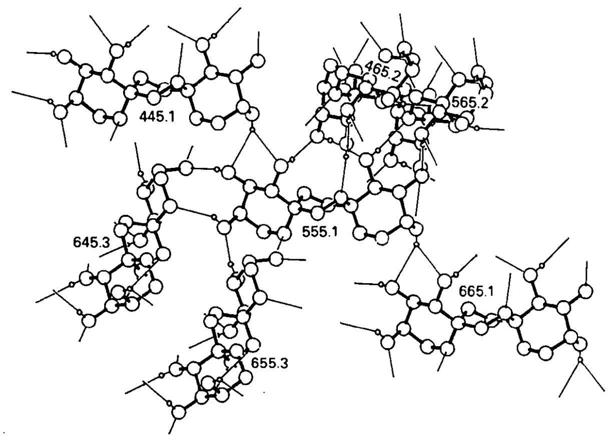

Fig. 2. A view of the structure as seen approximately along [210] showing the hydrogen-bond pattern. The symmetry code of the molecules is explained in the footnote to Table 3. H atoms not involved in hydrogen bonds have been omitted.

Table 3. *Hydrogen-bond geometry*

D—H···*A*	*D*···*A* (Å)	*D*—H (Å)	H···*A* (Å)	*D*—H···*A* (°)	Symmetry operation*
O(3)—H···O(2)	2·848 (2)	0·77 (3)	2·52 (3)	107 (2)	555·1
O(3)—H···O(14)	2·623 (2)	0·77 (3)	1·87 (3)	166 (3)	465·2
O(4)—H···O(5)	2·723 (3)	0·83 (3)	1·91 (3)	166 (3)	645·3
O(5)—H···O(4)	2·731 (3)	0·76 (3)	2·32 (3)	115 (3)	555·1
O(5)—H···O(6)	2·962 (3)	0·76 (3)	2·29 (3)	149 (3)	645·3
O(13)—H···O(1)	3·160 (2)	0·82 (3)	2·35 (3)	170 (3)	565·2
O(14)—H···O(13)	2·834 (3)	0·76 (3)	2·10 (3)	164 (3)	565·2
O(15)—H···O(3)	2·999 (3)	0·77 (3)	2·36 (3)	142 (3)	665·1
O(15)—H···O(4)	3·142 (3)	0·77 (3)	2·47 (3)	148 (3)	665·1

* The symmetry operation is performed on the acceptor O atoms. The first set of numbers specifies the lattice translations, *e.g.* 465·2 is $-a+b$ from 555·2. The last digit indicates one of the following symmetry operations: (1) x, y, z, (2) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (3) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

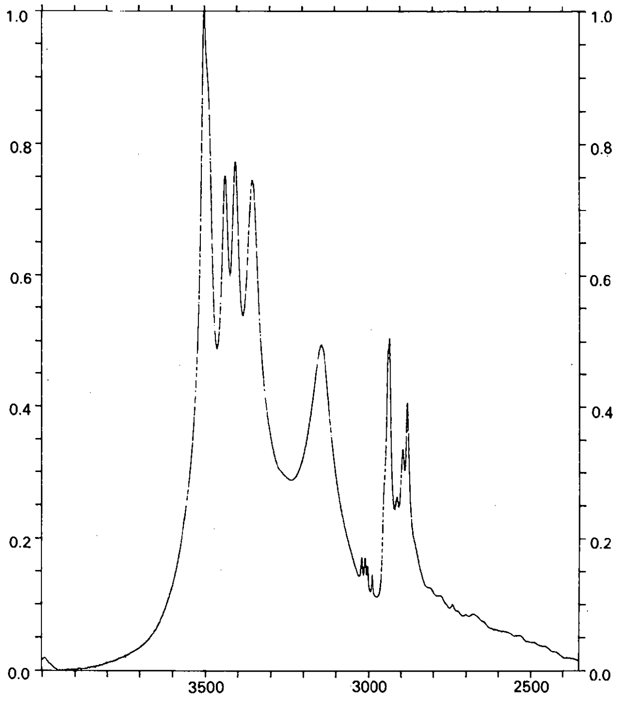

Fig. 3. IR absorption (normalized relative absorbance) in the 4000–2400 cm^{-1} region.

All hydroxyl groups are involved as donors in intermolecular hydrogen bonds (Table 3, Fig 2) of varying strength as is exemplified by the range of O···O distances which lie between 2·623 (2) and 3·160 (2) Å. Two bonds should at best be considered as very weak interactions because of the relatively large O···O separations, O(13)—H···O(1)($\frac{1}{2}+x, 1\frac{1}{2}-y, -z$), 3·160 (2) and O(15)—H···O(4)($1+x, 1+y, z$), 3·142 (3) Å.

The O(3)—H···O(14)($-\frac{1}{2}+x, 1\frac{1}{2}-y, -z$) hydrogen bond is very short, 2·623 (2) Å, and its geometry compares well with the strong hydrogen bonds in carboxylic acid dimers. Accordingly, it may be expected that the IR region between 4000 and 2400 cm^{-1} will display some noticeable features. As Fig. 3 shows, the spectrum reveals at least five sharp absorption maxima in that region of which the one at 3500 cm^{-1} clearly has a shoulder at the low-wavenumber side. The second derivative spectrum shows two peaks at 3502 and 3486 cm^{-1} respectively. These two peaks are tentatively assigned to the very weak hydrogen bonds O(13)—H···O(1) and O(15)—H···O(4). Investigations are in progress to assign the other maxima to the individual hydrogen-bond interactions.

With the exception of O(15)—H all hydroxyl-group O atoms act as hydrogen-bond acceptors and three hydroxyl groups donate to ether O atoms O(1), O(2) and O(6). There are three bifurcated hydrogen bonds; two are of the asymmetric type and one is of the symmetric type according to the classification of Newton, Jeffrey & Takagi (1979), as Table 3 shows. These three configurations are nearly planar, as follows from the sum of angles around the H atoms: for the bifurcated bonds involving the donor O atoms O(3), O(5) and O(15) these sums are 360 (4), 358 (4) and 360 (4)° respectively.

Each molecule is connected to six surrounding molecules by 14 hydrogen bonds, thus constituting a closely knit three-dimensional network.

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Structure of the Pyridine Adduct of Dithiophosphoryl Monochloride

BY M. T. AVERBUCH-POUCHOT

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'Université Joseph Fourier, BP 166*X*, 38042 *Grenoble CEDEX, France*

AND M. MEISEL

Zentralinstitut für anorganische Chemie der Akademie der Wissenschaften der DDR, Rudower Chaussee 5, *DDR*-1199 *Berlin, German Democratic Republic*

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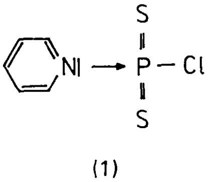
Abstract. $C_5H_5N.PS_2Cl$ (1), $M_r = 209\cdot66$, triclinic, $P\bar{1}$, $a = 9\cdot105$ (7), $b = 7\cdot954$ (6), $c = 6\cdot541$ (5) Å, $\alpha = 107\cdot89$ (1), $\beta = 101\cdot85$ (1), $\gamma = 78\cdot18$ (1)°, $V = 436$ (1) Å^3, $Z = 2$, $D_x = 1\cdot597$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0\cdot5608$ Å, $\mu = 0\cdot513$ mm^{-1}, $F(000) = 212$, $T = 295$ K, final $R = 0\cdot037$ for 1693 unique reflections. The most striking feature of the molecular structure of (1) is the remarkably long P—N bond (1·849 Å) which is, as far as is known, the longest P—N distance found in a compound containing tetrahedrally coordinated phosphorus. This results in the formation of a strongly distorted tetrahedron with the PS_2Cl group forming a relatively flat trigonal pyramid.

Introduction. The compound $C_6H_5N.PS_2Cl$ can be formulated either as a donor stabilized dithiomonometaphosphoryl chloride (1) or as a resonance stabilized zwitterionic pyridinium chlorodithiophosphinate betaine (2) (Meisel & Grunze, 1968; Meisel 1986):



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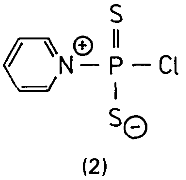

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