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Structure of 3,4,5-Tri-O-acetyl-1-deoxy-1-[(2,2-dimethoxycarbonylvinyl)amino]-β-D-fructopyranose

BY M. J. DIÁNEZ, A. LÓPEZ-CASTRO AND R. MÁRQUEZ

Departamento de Optica y Sección de Física del Departamento de Investigaciones Físicas y Químicas del CSIC, Universidad de Sevilla, Spain

Abstract. $C_{18}H_{25}NO_{12}$, $M_r = 447.4$, monoclinic, $P2_1$, $a = 8.879$ (2), $b = 7.375$ (3), $c = 16.990$ (2) Å, $\beta = 93.15$ (1)°, $V = 1110.9$ (5) Å^3, $Z = 2$, $D_m = 1.32$, $D_x = 1.33$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.1065$ mm^{-1}, $F(000) = 472$, $T = 300$ K, final $R = 0.070$ for 2026 observed $[I \geq 2\sigma(I)]$ independent reflections. Owing to the push–pull effect, the C=C bond distance is as long as 1.393 (8) Å and the twist angle around this bond is -174.2 (6)°. The sugar has a β-D configuration and the bond lengths and angles in the pyranose ring are normal. The two C—O glycosidic bond lengths are not equal [1.446 (9), 1.413 (7) Å], the shorter involving the anomeric carbon. The pyranose ring is in the chair conformation. The molecule has an intramolecular hydrogen bond between the NH and CO groups in the Z configuration, adopting the chelated form. The molecules are linked by van der Waals forces; additionally, one intermolecular hydrogen bond O—H⋯O through the OH group of the sugar and the carbonyl group in the configuration E is found.

Introduction. In the course of studying the behaviour of compounds with push–pull effects, and as a part of structural studies on enaminoesters and ketones ('enaminones'), the crystal structure of the title compound has been determined. A large number of substituted ethylenes are known where the C—C bond is significantly longer than in ethylene and the deviation from planarity is quite appreciable (Abrahamsson,

Rehnberg, Liljefors & Sandstrom, 1974; Ammon & Wheeler, 1975; Ammon, 1976; Adhikesavalu & Venkatesan, 1981, 1982; Diánez, López-Castro & Márquez, 1985). The two main factors which determine the geometry of the molecule are the conjugation push–pull effect and the steric strain in the planar state.

The compound of formula
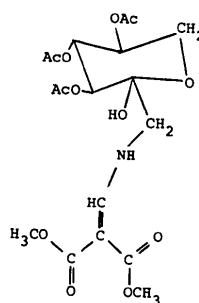
has been obtained, as a subproduct, from 1-deoxy-1-[2,2-dimethoxycarbonylvinyl)amino]-D-fructose and acetic anhydride in pyridine (275–295 K).

In this communication we report our findings on the molecular geometry as observed in the crystal structure.

Experimental. D_m measured by flotation. Single crystal in form of colourless prism with approximate dimensions $0.30 \times 0.31 \times 0.43$ mm used for intensity-data

collection; preliminary Weissenberg photographs indicated crystals are monoclinic with space group $P2_1$. Lattice parameters refined using 25 reflections in range $5 < \theta < 11°$. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode, $2\theta_{max} = 60°$ ($-12 < h < 12$, $k \leq 10$, $l \leq 23$). Two standard reflections (006 and 216) monitored every 100 reflections showed only statistical fluctuations. 2026 independent reflections measured [$I \geq 2\sigma(I)$], 1403 unobserved, Lorentz–polarization, no absorption or extinction corrections. Structure solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 286 E values ($E > 1.56$) used as input to MULTAN80 and correct set with highest figure of merit of 2.85 and residual value of 18.10 gave approximate positions of 21 of 31 non-H atoms, remaining atoms from difference synthesis; H atoms on C(sp^3) and C(sp^2) at calculated positions, H of OH group located in difference synthesis and refined with fixed B equal to those of bonded C atoms. Anisotropic weighted full-matrix least-squares refinement on F resulted in $R = 0.070$ and $wR = 0.065$, $w = 1/\sigma^2(F)$, $S = 3.35$. $\Delta/\sigma(\text{max.}) = 0.3$. Final difference Fourier synthesis showed $\Delta\rho = \pm0.3$ e Å^{-3}. The origin was defined by keeping the y coordinate of N(1) fixed. Scattering factors from International Tables for X-ray Crystallography (1962). Absolute configuration was established from chemical preparation. XRAY system (Stewart, Kundell & Baldwin, 1970) was used.*

Discussion. The positional and isotropic thermal parameters for non-H atoms are given in Table 1. Fig. 1 shows a schematic view of the molecule with the atom numbers, bond distances and angles. Fig. 2 is a projection on the (010) plane.

There is extensive electron delocalization involving the donor N(1) and the acceptor acetyl groups as reflected in the molecular dimensions. The C=C bond distance is 1.393 (8) Å, which is much longer than the C=C bond in ethylene [1.336 (2) Å (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965)]. There is a corresponding shortening of the N(1)—C(6) bond, 1.294 (7) Å, which is shorter than the 1.452 (2) Å reported for an N—C(sp^2) bond (Ammon, Mazzocchi, Regan & Colicelli, 1979). On the acceptor side, C(3)—C(2) and C(3)—C(4) are 1.442 (8) and 1.486 (9) Å respectively; one of them is shorter than the 1.487 (5) Å reported for a C(sp^2)—C(sp^2) single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). The carbonylvinylamino group has the Z configuration and is planar (maximum deviation 0.031 Å) and the

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*Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43367 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters* ($\times 10^4$) *for 3,4,5-tri-O-acetyl-1-deoxy-1-[(2,2-dimethoxycarbonylvinyl)-amino]-β-D-fructopyranose*

$$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(a_i, a_j).$$

	x	y	z	$U_{eq}(\text{Å}^2 \times 10^3)$
C(1)	2409 (10)	3383 (16)	7001 (4)	102 (4)
O(1)	1249 (5)	2565 (9)	6457 (2)	73 (2)
C(2)	1769 (8)	1821 (11)	5783 (4)	50 (3)
O(2)	3077 (5)	1766 (8)	5679 (3)	68 (2)
C(3)	572 (7)	1266 (9)	5227 (3)	43 (2)
C(4)	-1037 (7)	1136 (10)	5420 (4)	50 (3)
O(4)	-1459 (5)	989 (8)	6071 (2)	69 (2)
C(5)	-3544 (7)	1154 (14)	4917 (5)	83 (4)
O(5)	-1967 (5)	1250 (8)	4781 (3)	64 (2)
C(6)	935 (6)	769 (9)	4469 (3)	42 (2)
N(1)	2278 (5)	655	4214 (3)	49 (2)
C(7)	2583 (7)	204 (10)	3405 (3)	52 (3)
C(11)	2866 (7)	1900 (10)	2922 (4)	45 (2)
O(11)	1581 (5)	3019 (7)	2878 (2)	55 (2)
O	4103 (5)	2768 (7)	3323 (2)	46 (2)
C(21)	3275 (6)	1447 (10)	2083 (3)	38 (2)
O(211)	2030 (5)	619 (7)	1643 (2)	48 (2)
C(211)	2061 (8)	-1208 (11)	1538 (4)	56 (3)
O(212)	3056 (5)	-2149 (8)	1827 (3)	74 (2)
C(212)	766 (9)	-1868 (15)	1026 (5)	101 (4)
C(31)	3647 (7)	3224 (10)	1663 (3)	45 (2)
O(311)	4167 (5)	2780 (7)	896 (2)	56 (2)
C(311)	3550 (8)	3645 (11)	261 (4)	60 (3)
O(312)	2435 (7)	4532 (11)	299 (3)	114 (3)
C(312)	4382 (10)	3324 (13)	-448 (4)	86 (4)
C(41)	4940 (7)	4199 (10)	2114 (3)	49 (3)
O(411)	6272 (5)	3114 (8)	2085 (2)	55 (2)
C(411)	7391 (8)	3721 (12)	1660 (4)	70 (3)
O(412)	7331 (7)	5172 (10)	1347 (4)	164 (4)
C(412)	8591 (8)	2381 (14)	1566 (5)	88 (4)
C(51)	4534 (8)	4455 (11)	2964 (4)	53 (3)

methoxy and methoxycarbonyl groups are tilted by 3.9 (10) and 24.7 (8)° respectively. Torsion angles around C(3)—C(6) are −174.2 (6) and 4.0 (10)°, which indicates quantitatively the importance of this distortion.

The acetyl groups are planar [maximum deviation 0.027 (7) Å]. This planarity allows the torsion angles H—C$_{(rings)}$—O—C$_{(acetate)}$ to be used as a measure of the acetate orientation with respect to the adjacent C—H$_{(ring)}$. In the three cases the torsion angles are 3.15 (10), −12.36 (10), 4.27 (10)°. The C—C distances in the pyranose ring are in the range 1.520 (8)–1.537 (9) Å, in good agreement with those observed for related structures (Jeffrey & French, 1978); more interesting are the glycosidic C—O linkages: C(51)—O is significantly longer than C(11)—O, the shortening of the latter being characteristically associated with the anomeric C(11) atom (Jeffrey & French, 1978; Taga, Sumiya, Osaki, Utamura & Koizumi, 1981). The ring C—O bonds have a mean value of 1.430 (9) Å, while the exocyclic C—O lengths, excluding the C—OH bond of 1.407 (8) Å, having a mean of 1.437 (8) Å, are longer than the average value of 1.426 Å obtained for 23 non-acetylated glucosyl residues (Avenel, Neuman & Gillier-Pandraud, 1976).

The interior and exterior ring angles are in the range 106.9 (5)–112.1 (6)°, consistent with the expected high degree of tetrahedrality.

$C_{18}H_{25}NO_{12}$

The angles at the O atoms linked to the acetate groups have a mean of 118·3 (6)°, which is similar to the mean value of 118 (1)° observed in β-D-(1→4)-xylobiose hexaacetate (Leung & Marchessault, 1973). The three O—C(=O)—CH$_3$ angles are 112·4 (6), 112·4 (7) and 113·5 (7)°, which also agree well with those previously observed in β-D-(1→4)-xylobiose hexaacetate (Leung & Marchessault, 1973) and 3-O-acetyl-4-thiothymidine (Saenger & Suck, 1971), although according to Schweizer & Dunitz (1982) the expected value for the O—CO—C angle is 111°.

The molecular conformation of the pyranose ring in the crystal has been examined in terms of asymmetry parameters (Nardelli, 1983) and puckering parameters (Cremer & Pople, 1975) for the atomic sequence O, C(11), C(21), C(31), C(41) and C(51) are $\theta = 175$ (1)°, $\varphi = -65$ (7)°, $Q = 0.58$ (1) Å. The asymmetry parameters are $\Delta C_s[C(21)] = 0.010$ (3) and ΔC_2-[C(21)—C(11)] = 0.006 (3), so the molecular conformation is a chair, $^4C_1$. The C(7) substituent is equatorial and the O(11), O(211), O(311) and O(411) are axial.

The structure consists of a three-dimensional network of molecules linked by one intermolecular hydrogen bond [O(11)—H···O(4) $(-x, y + \frac{1}{2}, -z + 1)$ = 2·832 (7), O(11)—H = 1·06 (7), H···O(4) = 1·82 (7) Å, O(11)—H···O(4) = 160 (5)°]. There is one intramolecular hydrogen bond [N(1)—H···O(2) = 2·680 (6), N(1)—H = 1·00 (5), H···O(2) = 1·96 (4) Å, N(1)—H···O(2) = 126 (2)°] showing a chelated structure.

Fig. 1. View of the molecule with atom numbering, bond lengths (Å) and angles (°); e.s.d.'s are 0·007–0·011 Å and 0·5–0·8°.

C(21)—C(11)—C(7) = 111.5
O(11)—C(11)—O = 112.2

Fig. 2. Projection on the (010) plane.

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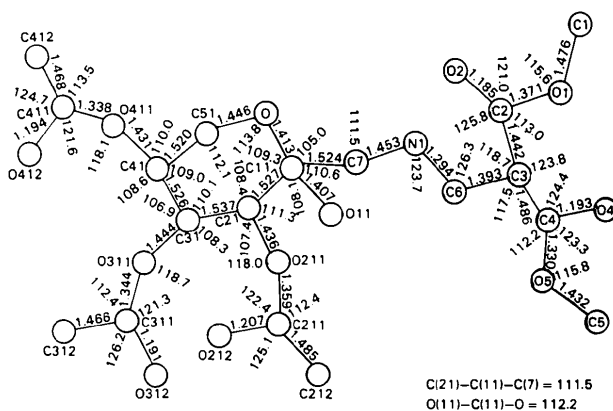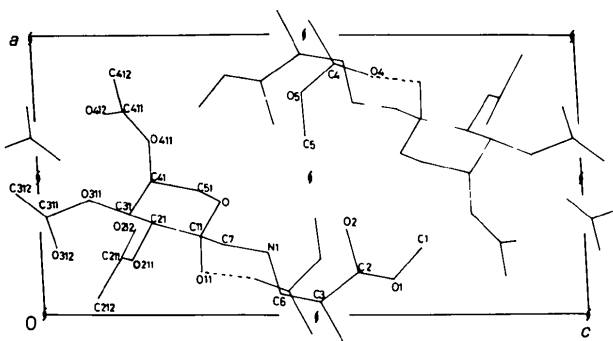TAGA, T., SUMIYA, S., OSAKI, K., UTAMURA, T. & KOIZUMI, K. (1981). *Acta Cryst.* B37, 963–966.