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Structure of Allyl 1-Deoxy-1-[(1-methyl-2-benzoylviny)amino]- α -D-fructofuranoside

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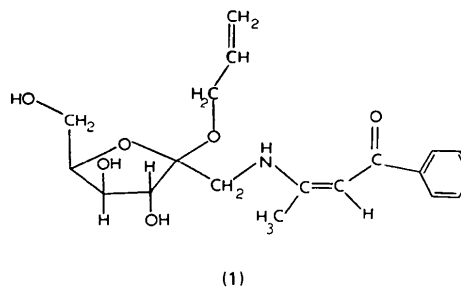
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Abstract. $C_{19}H_{25}NO_6$, $M_r = 363.4$, orthorhombic, $P2_12_12_1$, $a = 11.946$ (2), $b = 18.786$ (4), $c = 8.366$ (2) Å, $V = 1877.5$ (7) Å³, $Z = 4$, $D_x = 1.29$, $D_m = 1.29$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.089$ mm⁻¹, $F(000) = 776$, room temperature, final $R = 0.09$, $wR = 0.07$ for 1324 observed [$I > 2\sigma(I)$] reflections. The C=C bond distance is as long as 1.398 (10) Å but the twist angle around this bond is 1.6 (10)°. The sugar has an α -D-configuration and bond lengths and angles of the furanose ring are normal. The two C—O glycosidic bond lengths, 1.464 (9) and 1.407 (8) Å, are not equal, owing to the anomeric effect. The furanose ring is in the twist ²_T conformation. The molecule has an intramolecular H bond between the NH and CO groups adopting the chelate form. The molecules are linked by van der Waals forces; additionally there is one intermolecular H bond between the furanose and carbonyl groups.

Introduction. A variety of substituted ethylenes have C=C bonds significantly longer than the bond in ethylene [1.336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965; Kuchitsu 1966], e.g. trivinylborane, 1.370 (6) Å (Foord, Beagley, Reade & Steer, 1975). In olefins substituted with electron-releasing and electron-withdrawing groups in the vicinal positions such lengthening of the C=C bond is more pronounced with low barriers to rotation, e.g. dimethyl (dimethylaminomethylene)malonate, 1.380 (5) Å (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973); α -(*p*-bromobenzoyl)- β , β' -bis(methylthio)acrylonitrile, 1.369 (7) Å, *p*-bromobenzoyl(1,3-dimethylimidazolidinylidene)acetonitrile, 1.448 (4) Å (Abrahamsson, Rehnberg, Liljefors & Sandstrom, 1974). X-ray crystallographic results on a few other polarized ethylenes and related compounds have been reported (Shimanouchi, Ashida,

Sasada & Kakudo, 1967; Ammon & Plastas, 1971; Hazell & Mukhopadhyay, 1980; Adhikesavalu & Venkatesan, 1981; Diánez, López-Castro & Márquez, 1985*a,b*). In this paper we report X-ray results for allyl 1-deoxy-1-[(1-methyl-2-benzoylviny)amino]- α -D-fructofuranoside (1).



Samples kindly provided by Professor Gómez-Sánchez, University of Seville, Spain, were obtained by reaction with allylic alcohol in HCl of 1-deoxy-1-[(1-methyl-2-benzoylviny)amino]- α -D-fructofuranose (Gómez-Sánchez & Borrachero, 1984; Gómez-Sánchez, Garcia & Pascual, 1986; Diánez, López-Castro, Gómez-Sánchez, Garcia & Gasch, 1987). The structure determination was undertaken to confirm the identity of (1) and to determine its conformation, which has aroused interest as an 'enaminone', as well as for the bulky substituent (allyl deoxyfructofuranose group).

Experimental. D_m measured by flotation. Single crystal in form of colourless prism with approximate dimensions 0.30 × 0.31 × 0.43 mm used for intensity-data collection; preliminary Weissenberg photographs indicated crystals are orthorhombic with space group

P2₁2₁2₁. Lattice parameters refined using 25 reflections in range $4 < \theta < 12^\circ$. Enraf-Nonius CAD-4 diffractometer with graphite monochromator and Mo K α radiation. $\omega/2\theta$ mode, $2\theta_{\max} = 60^\circ$ ($h \leq 15$, $k \leq 24$, $l \leq 11$). 2601 independent reflections measured, $R_{\text{int}} = 0.01$ from merging 67 equivalent reflections, $I > 2\sigma(I)$, 1324 unobserved. Two standard reflections ($\bar{1}32$ and $1\bar{3}\bar{2}$) monitored every 100 reflections showed only statistical fluctuations. Lorentz-polarization, no absorption or extinction corrections. Structure solved by direct methods, MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 250 E values ($E > 1.49$) used as input to MULTAN80 and correct set with the highest figure of merit of 2.99 and residual value of 17.87 gave approximate positions of 23 of the 26 non-H atoms, remaining atoms from difference synthesis. Refinement on F by full-matrix least squares. H atoms included at calculated positions except those of OH groups that were located from difference Fourier synthesis. All non-H atoms refined using anisotropic temperature factors and isotropic for H atoms (corresponding to those of carrier atoms). Refinement produced convergence with $R = 0.09$, $wR = 0.07$; convenient weighting scheme to obtain flat dependence of $\langle w\Delta F \rangle$ vs $\langle F \rangle$ and vs $\langle (\sin\theta)/\lambda \rangle$ (Martínez-Ripoll & Cano, 1975), $S = 0.85$. Δ/σ (max.) = 0.5. The refinement was sluggish. Residual electron density in final difference map $\Delta\rho = \pm 0.5 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1962). Calculations performed with the XRAY70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970) and PARST (Nardelli, 1983a). The uncommonly high R factor and e.s.d.'s seem to be due to the disordered allyl group and to the shape and mediocre quality of the crystals.

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1.* Bond distances and angles are listed in Table 2. A view of the molecule with the numbering scheme of the atoms is shown in Fig. 1. The phenyl group is planar, with a maximum deviation from the best plane of 0.009 (9) Å. The attached atom C4 is at -0.078 (7) Å from the plane.

In the O-CH₂-CH=CH₂ group, the C111-C112 and C112-C113 bond lengths of 1.396 (15) and 1.226 (16) Å are much shorter than the normal C-C for single and double bonds respectively. It seems to us that this could result from the possible disordering for this group.

*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44564 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.


The central part of the molecule, the enamionone group  is planar, maximum deviation -0.031 (7) Å of C4 from the mean-squares plane

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

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

	x	y	z	U_{eq}
N	5222 (5)	1942 (3)	9121 (8)	52 (2)
O	3156 (4)	3138 (2)	7390 (6)	49 (2)
O4	7325 (5)	1661 (3)	8320 (7)	62 (2)
O11	5014 (4)	2933 (2)	6605 (7)	48 (2)
O21	2878 (5)	1597 (3)	7085 (7)	64 (2)
O31	3720 (4)	2616 (3)	3662 (6)	53 (2)
O51	1001 (5)	2506 (3)	6929 (8)	69 (2)
C	4291 (7)	2446 (5)	9081 (9)	55 (2)
C1	4260 (8)	1101 (5)	10817 (12)	75 (4)
C2	5273 (6)	1330 (4)	9907 (9)	50 (3)
C3	6240 (7)	911 (4)	9944 (9)	50 (3)
C4	7243 (7)	1105 (4)	9196 (9)	48 (3)
C5	8259 (7)	664 (4)	9419 (9)	47 (3)
C6	9192 (8)	777 (4)	8493 (11)	60 (3)
C7	182 (8)	391 (5)	8757 (11)	70 (4)
C8	235 (9)	-114 (5)	9950 (11)	74 (4)
C9	9316 (9)	-242 (5)	10872 (11)	65 (4)
C10	8352 (7)	147 (4)	10620 (10)	57 (3)
C11	4039 (6)	2642 (4)	7349 (9)	46 (3)
C21	3633 (6)	2056 (4)	6274 (9)	44 (3)
C31	2999 (6)	2467 (4)	4982 (9)	43 (2)
C41	2584 (7)	3132 (4)	5842 (9)	52 (3)
C51	1343 (7)	3139 (5)	6152 (10)	61 (3)
C111	5352 (9)	3601 (6)	7206 (13)	100 (5)
C112	5929 (10)	4033 (5)	6126 (12)	112 (6)
C113	6777 (10)	4392 (6)	6304 (16)	151 (9)

Table 2. Bond distances (Å) and bond angles ($^\circ$)

O-C11	1.407 (8)	C31-C41	1.524 (10)
O-C41	1.464 (9)	C21-C11	1.502 (10)
O11-C11	1.429 (8)	C2-C1	1.493 (12)
O11-C111	1.410 (11)	C11-C	1.525 (10)
O31-C31	1.428 (8)	C5-C10	1.401 (10)
O21-C21	1.420 (9)	C5-C6	1.373 (12)
O4-C4	1.279 (9)	C41-C51	1.505 (11)
N-C2	1.325 (9)	C10-C9	1.380 (13)
N-C	1.461 (10)	C6-C7	1.404 (13)
O51-C51	1.415 (10)	C9-C8	1.363 (14)
C4-C3	1.400 (11)	C8-C7	1.378 (13)
C4-C5	1.481 (11)	C111-C112	1.396 (15)
C3-C2	1.398 (10)	C112-C113	1.226 (16)
C31-C21	1.529 (10)		
C11-O-C41	108.8 (5)	C21-C11-C	117.1 (6)
C11-O11-C111	114.7 (6)	O11-C11-C	110.2 (6)
C2-N-C	127.4 (6)	O-C11-C	106.5 (5)
O4-C4-C5	117.7 (6)	C4-C5-C6	120.4 (7)
O4-C4-C3	122.2 (7)	C4-C5-C10	122.8 (7)
C3-C4-C5	119.9 (6)	C10-C5-C6	116.5 (7)
C4-C3-C2	123.4 (7)	O-C41-C31	105.7 (5)
O31-C31-C41	113.6 (6)	C31-C41-C51	114.1 (6)
O31-C31-C21	110.2 (5)	O-C41-C51	107.8 (6)
C21-C31-C41	103.9 (6)	C5-C10-C9	122.8 (8)
O21-C21-C31	109.2 (5)	N-C-C11	109.1 (6)
C31-C21-C11	102.3 (6)	C5-C6-C7	120.9 (8)
O21-C21-C11	111.3 (6)	O51-C51-C41	110.8 (7)
N-C2-C3	122.4 (6)	C10-C9-C8	119.4 (8)
C3-C2-C1	119.7 (7)	C9-C8-C7	119.6 (9)
N-C2-C1	117.7 (6)	C6-C7-C8	120.5 (8)
O11-C11-C21	106.4 (5)	O11-C111-C112	115.3 (9)
O-C11-C21	104.9 (5)	C111-C112-C113	130.4 (11)
O-C11-O11	111.5 (5)		

determined by all the atoms of this group. The N—C2 bond distance of 1.325 (9) Å is much shorter than the value of 1.452 (2) Å reported by Ammon, Mazzocchi, Regan & Colicelli (1979), and indicates partial double-bond character; the planar conformation for this group also indicates that the state of hybridization of the N atom is sp^2 . The C2=C3 bond length is 1.398 (10) Å [normal double bond in ethylene 1.336 (2) Å (Bartell, *et al.*, 1965)], and the twist angle around this bond is 1.6 (10)°. The low twist angle is due to the strong intermolecular H bonding between the NH and CO groups. Another consequence of the intramolecular H bonding is that the carbonyl group is *syn*, although these groups could be disposed in an *anti* conformation (Dewar & Haselbach, 1970). The C1—C2 and C4—C5 bond lengths, 1.493 (12) and 1.481 (11) Å, agree with the value given for the sp^2 — sp^2 single-bond distance, 1.487 (5) Å (Shmueli *et al.*, 1973). The C4=O4 bond length of 1.279 (9) Å is larger than the normal C=O bond, 1.23 (1) Å (*International Tables for X-ray Crystallography*, 1962). It could be attributed to the atom O4 being H-bonded to N. Examples are known where the C=O bond is lengthened due to hydrogen bonding (Craven, Cusatis, Garland & Vizzini, 1973; Ramani, Venkatesan & Marsh, 1978). The conjugation has resulted in the shortening of the N—C2, C2—C3, C1—C2, C3—C4 and C4—C5 bonds as expected and the lengthening of C4—O4.

In the furanose group the bond distances and angles are in good agreement with those in analogous compounds. However, the asymmetric endocyclic C—O bond lengths C41—O = 1.464 (9) and C11—O = 1.407 (8) Å show clearly the anomeric effect. The conformation of the five-membered ring can be described in terms of the pseudorotation phase angle, P , and the maximum torsion angle, τ_m , which are calculated from the endocyclic torsion angles* (Altona

& Sundaralingam, 1972). The values of P and τ_m are -47.5 and 42.8° respectively. The furanose ring has an unsymmetrical twist conformation 3T with approximate C_2 symmetry parameters $\Delta C_2(C41) = 0.005$ (3) (Nardelli, 1983*b*). The twofold axis passes through the atom C41 and bisects the C11—C21 bond. We note that O11, O21 and O31 are in axial positions and C and C51 in quasi-equatorial positions.

The molecule has two intramolecular hydrogen bonds: C111...O = 2.768 (2), H2C111...O = 2.32 Å and C111—H...O = 104° , and N...O4 = 2.653 (8), HN...O4 = 1.87 Å and N—H...O4 = 131° . The last one confirms the chelate structure characteristic of these compounds (Vega, Diáñez, López-Castro & Márquez, 1984).

Packing of the molecules is governed by van der Waals contacts and an intermolecular O—H...O hydrogen bond [O31...O4 ($x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$) = 2.715 (8), H...O4 = 1.87 Å and O31—H...O4 = 138°].

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* See deposition footnote.

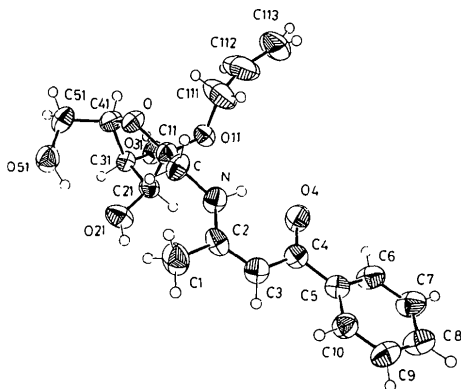


Fig. 1. A view of the molecule showing the atom-numbering scheme.

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Structure of the Product* Formed by the Addition of 4-Phenyl-3H-1,2,4-triazole-3,5(4H)-dione to Dimethyl 7H-Benzocycloheptene-7,7-dicarboxylate

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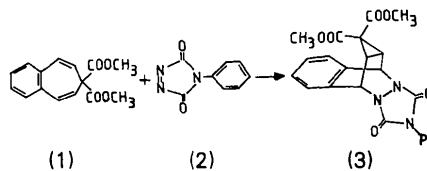
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Abstract. C₂₃H₁₉N₃O₆, $M_r = 433.4$, monoclinic, $P2_1/c$, $a = 12.166$ (5), $b = 13.857$ (5), $c = 12.331$ (5) Å, $\beta = 91.84$ (3)°, $V = 2078$ (2) Å³, $Z = 4$, $D_x = 1.385$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.95$ cm⁻¹, $F(000) = 904$, $T = 295$ K, $R = 0.057$ for 1614 unique observed reflections. The observed bond lengths and bond angles in the cyclopropane ring indicate the presence of a HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) interaction between the cyclopropane and one methoxycarbonyl group.

Introduction. There is much evidence to suggest that cycloheptatriene is in equilibrium with its valence isomer, norcaradiene (Maier, 1967; Kessler, 1972; Balci, 1982). The existence of unsubstituted norcaradiene in equilibrium has been proposed from cycloaddition reactions forming norcaradiene-type adducts. For example, 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) reacts with 7-substituted cycloheptatrienes to give only norcaradiene adducts (Adam, Balci & Pietrzak, 1979). In all cases it has been assumed that dienophiles react with the norcaradiene structure which is in equilibrium. The possibility that norcaradiene adducts can also be formed by a $(2\pi+2\pi+2\pi)$ -cycloaddition (homo-Diels–Alder addition) has never been considered (Atasoy &

Balci, 1986). To investigate this we synthesized the 7,7-dimethoxycarbonyl-7H-benzocycloheptene (1) which cannot equilibrate with its norcaradiene isomer, and subjected it to PTAD (2). We isolated the title compound (3) in a yield of 30%. The preparation, selected properties and a preliminary report of the structure have been published (Atasoy, Balci & Büyükgüngör, 1987). Here we describe the detailed X-ray analysis of this compound.



Experimental. Prepared by the method of Atasoy, Balci & Büyükgüngör (1987), needle-like transparent crystals, $0.7 \times 0.2 \times 0.02$ mm, Syntex R3 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from setting angles of 18 reflections, intensity data measured by ω -scan technique, variable scan speed: max. 12, min. 2° min^{-1} , scan range from 0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$, background/scan ratio 0.5; 3760 reflections measured, $4.5 \leq 2\theta \leq 43^\circ$, hkl range $-12, 0, -11$ to $12, 14, 12$, 1614 unique reflections considered observed, $I \geq 3\sigma(I)$, two check reflections at intervals of 100; variation $\pm 1.5\%$; Lorentz and

* Dimethyl 10,12-dioxo-11-phenyl-9,11,13-triazapentacyclo-[6.5.3.0^{2,7}.0^{9,13}.0^{14,16}]hexadeca-2(7),3,5-triene-15,15-dicarboxylate.