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Structure of 2-[(2,2-Diacetylvinyl)amino]-2-deoxy-α-D-glucopyranose, $C_{12}H_{19}NO_7$

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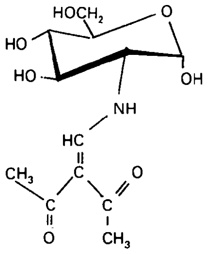
Abstract. $M_r = 289{\cdot}29$, monoclinic, $P2_1$, $a = 12{\cdot}495$ (2), $b = 4{\cdot}632$ (1), $c = 12{\cdot}391$ (2) Å, $\beta = 93{\cdot}9$ (1)°, $V = 715{\cdot}5$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·104 mm^{-1}, $F(000) = 308$, $T = 300$ K, final $R = 0{\cdot}052$ for 1317 observed $[I > 2\sigma(I)]$ independent reflections. Owing to the push–pull effect, the C=C bond distance is as long as 1·407 (9) Å and the twist angle around this bond is −179·0 (7)°. The molecule has an intramolecular hydrogen bond between the N and O atoms of the amino and one carbonyl group. The packing of the molecules is governed by four hydrogen bonds and van der Waals contacts.

Introduction. As part of structure studies on enamino-esters and ketones ('enaminones') the crystal structure of the title compound (I), obtained from D-glucosamine, 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). The two main factors which determine the geometry of the molecule are (i) the conjugation push–pull effect and (ii) the steric strain in the planar state. In this paper we report our findings on the molecular geometry as observed in the crystal structures.



(I)

Experimental. D_m measured by flotation. Single crystal in form of colourless prism with approximate dimensions 0·18 × 0·40 × 0·23 mm used for intensity-data collection; preliminary Weissenberg photographs indicated that the crystals are monoclinic with space group $P2_1$. Lattice parameters refined using 25 reflections in the range $5 < \theta < 11°$. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode, $2\theta_{\max} = 60°$ $(-17 \le h \le 17, k \le 6, l \le 17)$. Two standard reflections (006 and $00\bar{6}$) monitored every 100 reflections showed only statistical fluctuations. 1588 independent reflections measured, $R_{\rm int} = 0{\cdot}012$ from 58 merging equivalent reflections, $I > 2\sigma(I)$. Lorentz–polarization but no absorption or extinction corrections. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 230 E values ($E > 1{\cdot}40$) used as input to *MULTAN*80 and the correct set with the highest figure of merit of 2·7779 and residual value of 14·83 gave approximate positions of the 20 non-hydrogen atoms. Scattering factors from *International Tables for X-ray Crystallography* (1962). Full-matrix least-squares refinement based on F of the non-hydrogen atoms with isotropic temperature factors and unit weights gave $R = 0{\cdot}10$, with anisotropic temperature factors and weighting scheme $w = 1/\sigma^2(F)$ $R = 0{\cdot}072$. A difference Fourier synthesis (calculated up to $\sin\theta/\lambda = 0{\cdot}7$ Å^{-1}) revealed positions of all H atoms. Further refinement with non-hydrogen atoms treated anisotropically and H atoms isotropically produced convergence with $R = 0{\cdot}052$, $wR = 0{\cdot}051$ and $S = 2{\cdot}09$. In final cycle H atoms were assigned isotropic thermal parameters equal to those of the bonded C atoms. A final difference Fourier synthesis showed $\Delta\rho = \pm 0{\cdot}3$ e Å^{-3}. $(\Delta/\sigma)_{\max} = 0{\cdot}05$. The origin was defined by keeping fixed the y coordinate of C(1). The absolute configuration was established from the chemical preparation. The *XRAY* system (Stewart, Kundell & Baldwin, 1970) was used.

Discussion. The positional and isotropic thermal parameters are given in Table 1.* Bond lengths and angles are given in Fig. 1 which shows a view of the molecule.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39793 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($Å^2 \times 10^3$)

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

	x	y	z	U_{eq} or U_{iso}
N(1)	5897 (3)	7576 (22)	2307 (3)	34 (1)
C(1)	8477 (5)	2793	896 (5)	79 (3)
C(2)	7560 (4)	4201 (25)	1426 (4)	42 (2)
C(3)	7704 (3)	5759 (23)	2430 (4)	35 (2)
C(4)	8717 (4)	5701 (24)	3098 (4)	45 (2)
C(5)	8828 (4)	7341 (27)	4126 (4)	61 (2)
C(6)	6848 (3)	7376 (23)	2811 (3)	35 (1)
O(2)	6650 (3)	4048 (22)	946 (3)	58 (2)
O(4)	9478 (3)	4341 (23)	2812 (4)	83 (2)
O	3254 (2)	11023 (21)	1983 (3)	35 (1)
O(11)	4127 (2)	7431 (22)	1045 (2)	41 (1)
O(31)	5073 (2)	6992 (21)	4420 (2)	33 (1)
O(41)	2758 (2)	6748 (22)	4398 (3)	40 (1)
O(61)	1532 (2)	12768 (21)	3238 (3)	45 (1)
C(11)	4244 (3)	9912 (23)	1670 (4)	32 (1)
C(21)	4976 (3)	9113 (22)	2683 (3)	29 (1)
C(31)	4377 (3)	7269 (23)	3452 (3)	27 (1)
C(41)	3291 (3)	8565 (22)	3680 (4)	30 (1)
C(51)	2663 (3)	9013 (23)	2585 (4)	31 (1)
C(61)	1548 (4)	10159 (24)	2639 (4)	38 (2)
H(N1)	579 (3)	648 (22)	172 (3)	33
H1(C1)	838 (5)	388	12 (5)	73
H2(C1)	829 (5)	70	81 (5)	73
H3(C1)	919 (5)	355	123 (5)	73
H1(C5)	948 (4)	861 (27)	412 (4)	52
H2(C5)	907 (4)	620 (27)	469 (4)	52
H3(C5)	826 (4)	845 (27)	437 (4)	52
H(C6)	694 (3)	838 (23)	352 (3)	33
H(O11)	377 (2)	808 (22)	34 (2)	38
H(O31)	485 (2)	523 (21)	474 (2)	32
H(O41)	238 (2)	499 (22)	408 (3)	38
H(O61)	83 (2)	1356 (21)	314 (3)	48
H(C11)	458 (3)	1142 (23)	118 (4)	33
H(C21)	523 (3)	1090 (22)	305 (3)	28
H(C31)	424 (3)	535 (23)	310 (3)	27
H(C41)	339 (3)	1057 (22)	404 (4)	30
H(C51)	260 (3)	718 (23)	219 (4)	33
H1(C61)	120 (4)	1027 (24)	184 (4)	36
H2(C61)	109 (4)	866 (24)	292 (4)	36

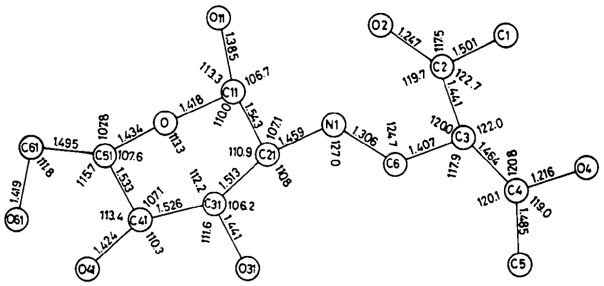

Fig. 1. Interatomic distances (Å) and angles (°) (mean e.s.d.'s 0·008 Å and 0·4°).

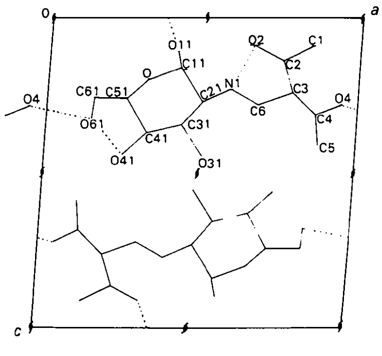

Fig. 2. The molecular packing viewed along the y axis. For details of hydrogen bonds (broken lines) see Table 2.

Table 2. *Geometry of the short contacts involving hydrogen atoms*

D—H···A	D···A (Å)	D—H (Å)	H···A (Å)	D—H···A (°)
N(1)—H···O(2)	2·575 (10)	0·89 (7)	1·87 (7)	135 (3)
C(1)—H···O(4)	2·708 (8)	1·02 (6)	2·00 (6)	124 (1)
O(11)—H···O(2^{iv})	2·697 (6)	1·00 (4)	1·70 (4)	171 (2)
O(31)—H···O(31^{i})	2·739 (12)	0·96 (8)	1·82 (8)	159 (2)
O(41)—H···O(61^{ii})	2·735 (10)	1·00 (8)	1·76 (6)	161 (4)
O(61)—H···O(4^{iii})	2·683 (6)	0·95 (4)	1·74 (3)	168 (6)

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+1$; (ii) $x, y-1, z$; (iii) $x-1, y+1, z$; (iv) $-x+1, y+\frac{1}{2}, -z$.

(2,2-*Diacetylvinyl*)*amino group*. There is extensive electron delocalization involving the donor N(1) and the acceptors (acetyl groups) as reflected in the molecular dimensions. The C=C bond distance is 1·407 (9) 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, 1·306 (5) 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 1·441 (9) and 1·464 (6) Å respectively, which are 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 (diacetylvinyl)amino group is strictly planar except for one of the acetyl [C(2)O(2)C(1)] groups which is tilted by 9·4 (4)° with respect to the central moiety C(2)C(3)C(4)C(6)N(1) of the molecule and this is only due to the contacts N(1)—H···O(2) and C(1)—H···O(4). Torsion angles C(6)—C(3)—C(2)—O(2) −6·8 (11), C(6)—C(3)—C(2)—C(1) 170·8 (6), C(1)—C(2)—C(3)—C(4) −9·8 (10)° indicate quantitatively the importance of this distortion.

Glucopyranose ring. The mean bond lengths C—C 1·529 (9) Å and C—O 1·420 (10) Å and the mean angle of 110·3 (7)° in the ring are in good agreement with those found in analogous systems (Neuman & Gillier, 1983). The C(51)—O bond length of 1·434 (10) Å is generally about 0·02 Å longer than C(11)—O as a result of the anomeric effect (Jeffrey, Pople & Radom, 1974; Jeffrey, McMullan & Takagi, 1977). The conformation of the pyranose ring is a chair [mean torsion angle 58 (9)°; Cremer & Pople's (1975) puckering parameters indicate the atomic sequence in the ring: $\theta = 170{\cdot}9\ (9)°$, $\varphi = -116\ (5)°$, $q_2 = -0{\cdot}093\ (9)$ Å, $q_3 = -0{\cdot}579\ (9)$ Å, $Q = 0{\cdot}587\ (9)$ Å]. The N(1), O(31), O(41) and C(61) substituents are equatorial, while the C(11)—O(11) bond is axial. The twist angle around C(3)—C(6) is −179·0 (7)°.

Crystal packing and hydrogen bonding. The packing of the molecules in the unit cell is shown in Fig. 2. The structure consists of a three-dimensional network of molecules linked by hydrogen bonds. Details of the geometry of the short distances involving H atoms are given in Table 2. As can be seen, there are four intermolecular and one intramolecular [N(1)—H···O(2)] hydrogen bonds.

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Konformation von 2-Methyl-2-(4-nitrophenyl)-1,3-dithian, $C_{11}H_{13}NO_2S_2$

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Abstract. $M_r = 255{\cdot}35$, monoclinic, $P2_1/n$, $a = 11{\cdot}039\,(4)$, $b = 16{\cdot}942\,(6)$, $c = 6{\cdot}381\,(2)$ Å, $\beta = 91{\cdot}35\,(2)°$, $V = 1193{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}41$, $D_x = 1{\cdot}42$ Mg m^{-3}, $F(000) = 536$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}4$ mm^{-1}, $T = 293$ K, $R = 0{\cdot}036$ for 659 reflexions. The phenyl ring adopts the axial position and is orientated perpendicular to the mirror plane of the 1,3-dithiane ring. There are no unusual bond distances or angles.

Einleitung. Über die Konformationsanalyse von Heterocyclen informiert eine ausführliche Übersicht von Zefirov & Kazimirchik (1974). Die Konformation des sesselförmigen Cyclohexan findet man auch in 1,3-Dithian (Adams & Bartell, 1977), ebenso in 2-Phenyl-1,3-dithian (Kalff & Romers, 1966) mit äquatorial stehendem Phenylsubstituenten. Die Einführung eines zweiten Substituenten sollte dagegen im 2-Methyl-2-phenyl-1,3-dithian zu einer Bevorzugung der Konformation mit axialer Phenylgruppe führen, abgeleitet aus ^{1}H-NMR-spektroskopischen Kriterien (Langer & Lehner, 1975).

Experimentelles. Aus ethanolischer Lösung waren geeignete Kristalle gut erhältlich. Weissenberg- und Präzessionsaufnahmen ergaben über die Lauesymmetrie $2/m$ und die systematischen Auslöschungen $h0l$ mit $h + l = 2n + 1$ und $0k0$ mit $k = 2n + 1$ die Raumgruppe $P2_1/n$ (Nr. 14) (*International Tables for X-ray Crystallography,* 1952). Die genaue Bestimmung der Gitterkonstanten erfolgte durch Verfeinerung von 18 Reflexen einer Diffraktometer-Pulveraufnahme (Warczewski & de Wolff, 1974).

Zur Intensitätsbestimmung wurden alle Reflexe der 0. bis 5. Schicht eines nadelförmigen, nach [001] justierten Kristalls (0,15 × 0,12 × 1,5 mm) im Bereich $4° \leq 2\theta \leq 35°$ mit dem Zweikreisdiffraktometer (Weissenberg-Äquiinklinationsverfahren, Graphit-Monochromator, Mo $K\alpha$) in ω-Abtastung mit 0·01° pro Schritt registriert, bei höheren Schichten mit variablem ω-Bereich mit den empirisch ermittelten Werten $\Delta\omega(°) = 0{,}8 + 0{,}6\sin\mu/\tan(Y/2)$. Jeweils vor und nach der Abtastung eines Reflexes wurde der Untergrund bestimmt, nach jedem 50. wurde der Standardreflex gemessen. Bei stärkeren Reflexen konnten entsprechend der Vormessung Schwächungsfilter vorgeschaltet werden. Mit $I_o \geq 3\sigma(I)$ ergaben sich 1252 beobachtete Reflexe. Nach der Untergrundkorrektur wurden über Polarisations- und Lorentzfaktor Strukturfaktoren berechnet, die zu 659 symmetrieunabhängigen

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