outre, l'angle O···C=O (α) a une valeur proche de 100 à 110°. Enfin, l'atome O nucléophile montre une tendance à se placer dans le plan bissecteur de l'angle R_xCR_y. La plus courte distance intermoléculaire O···C qu'ils ont trouvée vaut 2,77 Å. Les valeurs des distances et des angles qui décrivent l'interaction C···O dans $C_6H_9NO_4$ sont en accord avec les conclusions de Bürgi *et al.*: si nous identifions R_x à O(71) et R_y à C(2), on trouve $\Delta = +0{,}011\ (2)$, $\alpha = 96{,}6°$, $\beta_3(\equiv \angle R_x\mathrm{CO}) = 90{,}8°$ et $\beta_4\ (\equiv \angle R_y\mathrm{CO}) = 83{,}2°$.

Les auteurs remercient MM les Professeurs J. Toussaint et J. Jadot pour l'intérêt qu'ils ont porté à ce travail.

Références

AHMED, F. R., HALL, S. R., PIPPY, M. E. & SAUNDERSON, C. P. (1967). NRC Crystallographic Programs for the IBM/360 System, National Research Council, Ottawa, Canada.

BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* B**30**, 1517–1527.

CRUICKSHANK, D. W. J. (1960). Dans *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Edité par R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

DUPONT, L., DIDEBERG, O. & WELTER, A. (1975). *Acta Cryst.* B**31**, 1018–1022.

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. (1970). *Acta Cryst.* B**26**, 765–770.

KAYUSHINA, R. L. & VAINSHTEIN, B. K. (1966). *Sov. Phys. Crystallogr.* **10**, 698–706.

KOCH, M. H. J. (1974). *Acta Cryst.* B**30**, 67–70.

KOETZLE, T. F., LEHMANN, M. S. & HAMILTON, W. C. (1973). *Acta Cryst.* B**29**, 231–236.

LAMOTTE, J., DUPONT, L. & DIDEBERG, O. (1977). *Acta Cryst.* B**33**, 409–412.

MAIN, P. (1970). Programme pour la réduction des données. Univ. of York, Angleterre.

PREWITT, C. T. (1967). *SFLS*. State Univ. of New York, Stoney Brook, Long Island, New York 11790, USA.

WELTER, A., MARLIER, M. & DARDENNE, G. (1977). *Phytochemistry*. Sous presse.

ZALKIN, A. & WARD, D. (1974). *HFINDR*, programme pour calculer les positions des hydrogènes (version modifiée). Lawrence Berkeley Univ., USA.

Acta Cryst. (1978). B**34**, 854–858

The Crystal and Molecular Structure of 2-Acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone, $C_8H_{11}NO_5$

BY ŽIVA RUŽIĆ-TOROŠ

'Ruder Bošković' Institute, PO Box 1016, 41001 *Zagreb, Yugoslavia*

AND F. LAZARINI

Department of Chemistry, University of Ljubljana, Murnikova 6, 61000 *Ljubljana, Yugoslavia*

(*Received* 23 *July* 1977; *accepted* 28 *September* 1977)

2-Acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone crystallizes in space group $P2_12_12_1$ with $a = 4{\cdot}904\ (1)$, $b = 7{\cdot}670\ (1)$, $c = 24{\cdot}148\ (3)$ Å, $Z = 4$. The structure was solved by direct methods and refined to an R of 0·058. The lactone ring is planar within experimental error. The molecules are linked in a three-dimensional network by intermolecular O(5)—H···O(7) (2·729), O(6)—H···O(5) (2·838) and N—H···O(1) (2·948 Å) hydrogen bonds.

Introduction

The crystal structure determination of 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone represents a continuation of our previous work on the structures of aminoacetylated unsaturated five-membered-ring lactones. The crystal structure of the *threo* isomer has already been published (Ružić-Toroš & Kojić-Prodić, 1976). The inhibitory activities of 2-acetamido-2,3-dideoxy-D-hex-2-enonolactones on 2-acetamido-2-dideoxy-β-D-glucosidase were tested. Only the *erythro* isomers are inhibitors, whereas the *threo* lactones are practically inactive. It was also observed that the 1,4-lactone inhibited 2-acetamido-2-deoxy-β-D-glucosidase more strongly than the 1,5-lactone (Pokorny, Zissis, Fletcher & Pravdić, 1975). The reason for the various inhibitory activities among these compounds was not obvious. It is very useful to make correlations between the molecular geometry and the inhibitory properties of these compounds and thus the crystal structure determination of the *erythro* isomer has been undertaken.

Experimental

Crystals of 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone are colourless prisms. Unit-cell dimensions were determined from oscillation photographs with Cu $K\alpha$ radiation. The precise values (Table 1) were then deduced from zero-layer rotation patterns of single crystals (about the *a* and *c* axes) taken in asymmetric (Straumanis) positions and indexed by means of corresponding Weissenberg photographs (Popović, 1974).

Table 1. *Crystallographic and physical data*

2-Acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone, $C_8H_{11}NO_5$

FW	201·18
Space group	$P2_12_12_1$
a	4·904 (1) Å
b	7·670 (1)
c	24·148 (3)
U	908·3 Å^3
D_c	1·472 g cm^{-3}
Z	4
μ(Cu $K\alpha$)	7·30 cm^{-1}
Crystal shape	Prismatic
Crystal dimensions	0·09 × 0·18 × 0·5 mm
$F(000)$	424

Table 2. *Final positional parameters* ($\times 10^4$) *for the non-hydrogen atoms*

	x	y	z
C(1)	−773 (12)	3200 (7)	606 (2)
C(2)	−333 (12)	1611 (7)	936 (2)
C(3)	−1851 (12)	1673 (7)	1390 (2)
C(4)	−3349 (12)	3368 (8)	1389 (2)
C(5)	−2651 (11)	4638 (7)	1852 (2)
C(6)	−3208 (13)	3945 (8)	2422 (3)
C(7)	1823 (12)	−1244 (7)	921 (2)
C(8)	3921 (15)	−2312 (8)	618 (3)
O(1)	265 (10)	3647 (5)	178 (2)
O(4)	−2650 (9)	4177 (5)	870 (2)
O(5)	189 (8)	5055 (5)	1824 (2)
O(6)	−5896 (10)	3281 (8)	2481 (2)
O(7)	521 (9)	−1769 (5)	1319 (2)
N	1484 (10)	389 (6)	720 (2)

The space group was determined from Weissenberg photographs recorded with Cu K radiation. Systematic absences indicated space group $P2_12_12_1$.

The intensities were collected on an Enraf–Nonius CAD-4 single-crystal automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation. Reflexions were scanned in the ω–2θ mode (2θ scan width = 0·6 + 0·2 tan θ). Intensities were measured in the range $1 < \theta < 90°$. 2274 reflexions were collected from the hkl and $hk\bar{l}$ octants and were averaged to give a set of 1137 reflexions. 201 of these were unobserved ($I \leq 2\sigma$). The data were corrected for variations in the intensity of the reference reflexions, and for Lorentz and polarization effects.

Structure determination and refinement

The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Overall temperature and scale factors were determined (Wilson, 1942) and used to compute normalized structure amplitudes by the routine *NORMAL* included in *MULTAN*. The solution was based on 250 reflexions with $|E| \geq 1{\cdot}2$. The E map corresponding to the solution with the best figure of merit (ABSFOM = 1·31) revealed the positions of 11 non-hydrogen atoms. The positions of the other three non-hydrogen atoms were located from the resulting Fourier synthesis. A full-matrix least-squares procedure minimizing $\Sigma w||F_o| - |F_c||^2$ with $w = 1/\sigma^2_{|F_o|}$ was used for the refinement. Heavy-atom coordinates, isotropic thermal parameters and a scale factor were refined to an R of 0·118. H atoms were located from a difference Fourier synthesis after a few cycles of anisotropic refinement (R = 0·081). In the final cycle, one scale factor, the atomic positional parameters and the anisotropic thermal parameters for the non-hydrogen atoms were varied. For H atoms the coordinates were taken from a difference Fourier synthesis and the isotropic thermal parameters were those of the bonded atoms. The final

Table 3. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters* ($\times 10^2$) *for the hydrogen atoms*

	x	y	z	U (Å^2)
H(3)	−188	85	170	3·7
H(4)	−525	315	140	3·8
H(5)	−349	573	178	2·6
H(6,1)	−300	490	270	4·7
H(6,2)	−210	280	255	4·7
H(8,1)	320	−335	44	5·1
H(8,2)	420	−156	24	5·1
H(8,3)	520	−235	90	5·1
H(N)	190	60	38	3·2
H(O5)	30	625	165	7·5
H(O6)	−675	390	220	7·1

Table 4. *Bond angles* (°)

O(1)–C(1)–O(4)	122·5 (5)	O(4)–C(4)–H(4)	109
O(1)–C(1)–C(2)	129·8 (5)	C(3)–C(4)–H(4)	109
O(4)–C(1)–C(2)	107·7 (4)	C(5)–C(5)–H(4)	108
C(1)–C(2)–C(3)	109·6 (5)	O(5)–C(5)–C(4)	109·1 (5)
C(1)–C(2)–N	116·6 (5)	O(5)–C(5)–C(6)	107·5 (5)
C(3)–C(2)–N	133·8 (5)	C(4)–C(5)–C(6)	113·9 (5)
C(2)–C(3)–C(4)	107·8 (5)	O(6)–C(6)–C(5)	112·9 (5)
C(2)–C(3)–H(3)	128	O(7)–C(7)–C(8)	124·0 (5)
C(4)–C(3)–H(3)	124	O(7)–C(7)–N	121·5 (5)
O(4)–C(4)–C(3)	105·0 (5)	C(8)–C(7)–N	114·4 (5)
O(4)–C(4)–C(5)	108·1 (5)	C(2)–N–C(7)	124·5 (5)
C(3)–C(4)–C(5)	116·5 (5)	C(1)–O(4)–C(4)	109·5 (4)

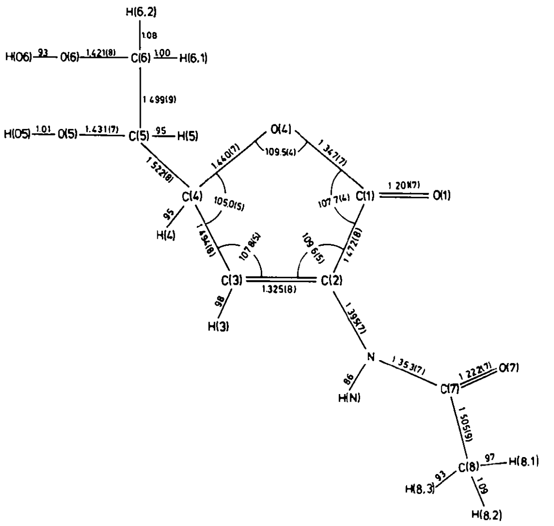


Fig. 1. The numbering of the atoms and bond lengths (Å).

agreement indices were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}058$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/|F_o|^2]^{1/2} = 0{\cdot}069$.

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

Table 5. *Displacements from the least-squares plane* (Å) *for the lactone group*

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

C(2)*	−0·014
C(1)*	−0·006
O(1)*	−0·039
O(4)*	0·025
C(4)*	0·034
C(3)	−0·013

Table 6. *Torsion angles* (°) *describing the conformations about* C(4)–C(5) *and* C(5)–C(6)

C(3)–C(4)–C(5)–O(5)	59·4 (6)
C(3)–C(4)–C(5)–H(5)	171
O(4)–C(4)–C(5)–O(5)	−58·4 (6)
O(4)–C(4)–C(5)–C(6)	−178·5 (5)
H(4)–C(4)–C(5)–C(6)	62
H(4)–C(4)–C(5)–H(5)	−66
C(4)–C(5)–C(6)–H(6,1)	−171
C(4)–C(5)–C(6)–H(6,2)	62
O(5)–C(5)–C(6)–O(6)	−172·7 (5)
O(5)–C(5)–C(6)–H(6,2)	−59
H(5)–C(5)–C(6)–O(6)	75
H(5)–C(5)–C(6)–H(6,1)	−44

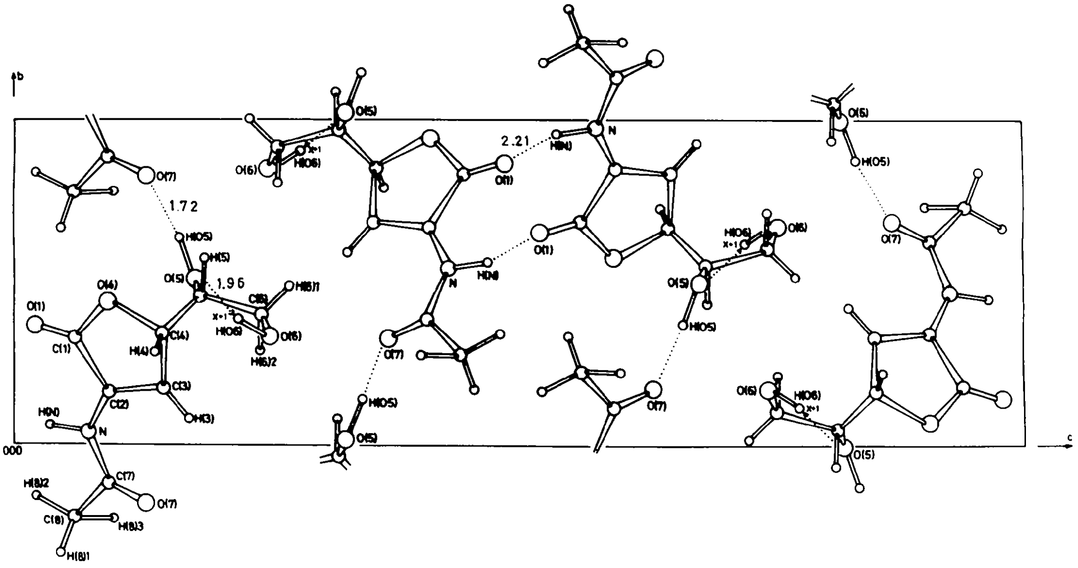


Fig. 2. A view of the crystal structure along **a** showing the packing arrangement and hydrogen bonds.

Table 7. *Hydrogen bonds*

X–H···Y	X···Y	X–H	H···Y	∠X–H···Y	Symmetry operation
O(5)–H(O5)···O(7)	2·729 (6) Å	1·01 Å	1·72 Å	177°	$x,y,z; x, y+1, z$
O(6)–H(O6)···O(5)	2·838 (7)	0·93	1·96	156	$x,y,z; x-1, y,z$
N–H(N)···O(1)	2·948 (6)	0·86	2·21	144	$x,y,z; x+\frac{1}{2}, \frac{1}{2}-y, -z$

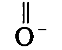
The calculations were carried out on the Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Positional parameters are listed in Tables 2 and 3.*

Description and discussion of the structure

The numbering of the atoms and the values of the bond lengths are shown in Fig. 1. The molecular packing and hydrogen bonds are illustrated in Fig. 2. Interatomic angles are listed in Table 4 and displacements of the atoms from the least-squares plane through the lactone group and ring are in Table 5. Dihedral angles defining the conformation about C(4)–C(5) and C(5)–C(6) are given in Table 6.

The atoms defining the lactone group are planar with a maximum deviation of 0·039 Å for O(1) (Table 5). The C(3) atom belonging to the lactone ring is displaced by 0·013 Å from the least-squares plane through the lactone group. Thus the lactone group and ring are both planar within the range of experimental error.

The conformation of the side chain about the C(4)–C(5) bond is 'staggered'; about the C(5)–C(6) bond the conformation is '*anti*' (Table 6). The bond lengths and angles [with the exception of internal angles at C(2) and C(3)] are comparable with the values for the relevant type of hybridization, and with those found in L-ascorbic acid (Hvoslef, 1968), and the *threo* isomer of this compound (Ružić-Toroš & Kojić-Prodić, 1976).

The C–C bond lengths are in the range 1·472–1·522 Å. The value of C(2)=C(3) [1·325 (8) Å] is equal to that in the *threo* isomer of this compound (Ružić-Toroš & Kojić-Prodić, 1976) and is comparable with 1·337 (6) Å (*International Tables for X-ray Crystallography*, 1968). The single bonds C(1)–C(2) [1·472 (8)] and C(3)–C(4) [1·494 (8) Å] are shortened compared with the standard value of 1·54 Å, owing to the influence of the C=O and C=C double bonds. However, they are normal for this structure. The asymmetry of the endocyclic C(1)–O(4) [1·347 (7)] and C(4)–O(4) [1·440 (7) Å] bonds observed in the present structure was also found in L-ascorbic acid (Hvoslef, 1968), γ-D-gulonolactone (Berman, Rosenstein & Southwick, 1971) and the *threo* isomer of this compound (Ružić-Toroš & Kojić-Prodić, 1976). This asymmetry can be interpreted by the valence resonance form  $\underset{\underset{O^-}{\|}}{-C}=C^+-C-$. Other single C–O bonds of 1·421 (8) and 1·431 (7) Å, and double C=O bonds of 1·201 (7) and 1·222 (7) Å are in the usual range. The C–N bonds are 1·353 (7) and 1·395 (7) Å.

The internal angles C–C–C, C–O–C and O–C–C are in the range 105·0 (4)–109·6 (5)°. The mean value of 107·9° is nearly equal to the calculated angle of 108° in a regular pentagon. The influence of five-membered-ring geometry on the values of bond angles in the lactone ring at C(1) [107·7 (4)°], C(2) [109·6 (5)] and C(3) [107·8 (5)°] is obvious. The same distortions are noticed in L-ascorbic acid (Hvoslef, 1968) and the *threo* isomer (Ružić-Toroš & Kojić-Prodić, 1976).

The molecules are connected by hydrogen bonds forming a three-dimensional network (Fig. 2 and Table 7). Both hydroxyl groups are involved in hydrogen bonds. The O(5) hydroxyl group acts as an acceptor in O(6)–H(O6)···O(5) [2·838 (7) Å] and as a donor to a carbonyl O atom in the O(5)–H(O5)···O(7) [2·729 (6) Å] hydrogen bond. The N atom in the acetamido group acts as a donor to the second carbonyl O forming the N–H···O(1) [2·948 (6) Å] hydrogen bond.

The intensities were collected at the Department of Chemistry, University of Ljubljana. The authors are grateful to Professor L. Golič for facilities placed at their disposal. We thank Dr N. Pravdić for the crystals and valuable discussion.

References

Berman, H. M., Rosenstein, R. D. & Southwick, J. (1971). *Acta Cryst.* B**27**, 7–10.

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.

Hvoslef, J. (1968). *Acta Cryst.* B**24**, 23–25.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33064 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., p. 276. Birmingham: Kynoch Press.
POKORNY, M., ZISSIS, E., FLETCHER, H. G. JR & PRAVDIĆ, N. (1975). *Carbohydr. Res.* **43**, 345–354.
POPOVIĆ, S. (1974). *J. Appl. Cryst.* **7**, 291–292.
RUŽIĆ-TOROŠ, Ž. & KOJIĆ-PRODIĆ, B. (1976). *Acta Cryst.* B**32**, 2333–2336.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. 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.
WILSON, A. J. C. (1942). *Nature* (*London*), **150**, 151–152.

Acta Cryst. (1978). B**34**, 858–862

Stereochemistry of Unsaturated Amino Sugars. III. The Crystal and Molecular Structure of Peracetylated 1,2-Dideoxy-D-*arabino*-aldopyranose, $C_{16}H_{21}O_9N$

BY BISERKA KOJIĆ-PRODIĆ

'Ruđer Bošković' Institute, PO Box 1016, 41001 *Zagreb, Yugoslavia*

AND V. ROGIĆ

Institute for Metallurgy, 44000 *Sisak, Yugoslavia*

(*Received* 27 *July* 1977; *accepted* 23 *September* 1977)

3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose crystallizes in space group $P2_12_12$ with $a = 11{\cdot}805$, $b = 18{\cdot}586$, $c = 8{\cdot}3196$ Å, $Z = 4$. The structure was solved by *MULTAN* and refined with a full-matrix least-squares procedure to $R = 0{\cdot}045$. The sugar ring exhibits an alternate sofa conformation; four C atoms and the ring O atom are coplanar and only one C atom is below this plane. The substituents are attached to C(3) in quasi-equatorial, and to C(4) and C(5) in equatorial positions. Owing to the absence of free hydroxyl groups, hydrogen bonds of the type O—H···O are not possible. In the crystal lattice the molecules are joined by van der Waals interactions only.

Introduction

3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose was synthesized (Pravdić & Fletcher, 1967; Pravdić, Franjić-Mihalić & Danilov, 1975) as the first representative of a new class of unsaturated amino sugars. The crystal structures of three compounds from this series have already been solved (Kojić-Prodić, Rogić & Ružić-Toroš, 1976; Rogić, Ružić-Toroš, Kojić-Prodić & Pravdić, 1977). The main interest of the structural study of the above series is the sugar-ring conformation. The presence of the double bond in these ring systems suggests a half-chair conformation. Indeed, it was found to be highly predominant in this series. The present structure determination, as part of this study, shows the sugar ring to be in an unusual alternate sofa conformation.

Experimental

The space group was determined as $P2_12_12$ from Weissenberg photographs recorded with Cu $K\alpha$ radiation. Cell constants were obtained by the least-squares procedure using the θ values for 19 reflexions in the interval $50{\cdot}2° < 2\theta < 57{\cdot}6°$ (at 18 °C) with Cu $K\alpha$ radiation. Crystal data are given in Table 1. Integrated intensities for 2151 independent reflexions with $\theta < 75°$ were measured on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation. The data were corrected for background, Lorentz and polarization effects.

Structure determination and refinement

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) using normalized structure amplitudes calculated by the *K*-curve method (Hauptman & Karle, 1953). The solution was based on 271 reflexions with $|E| \geq 1{\cdot}50$. The *E* map corresponding to the solution with the best figure of merit revealed the positions of all the non-hydrogen atoms. The H atoms were located from a difference Fourier map with the exception of H(8,2), H(10,3), H(12,3), and H(16,3). Their positions were calculated on stereo-