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SYNTHESIS OF ALKYL GLYCO-PYRANOSIDES AND -FURANOSIDES OF 2-AMINO-2-DEOXY-D-GLUCOSE. CRYSTAL STRUCTURE OF 2-DEOXY-2-[(4,4-DIMETHYL-2,6-DIOXOCYCLOHEXYLIDENEMETHYL)AMINO]-α-D-GLUCOPYRANOSE*,†

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ABSTRACT

The reaction of 2-amino-2-deoxy-D-glucose hydrochloride with 5,5-dimethyl-2-phenylaminomethylene-1,3-cyclohexanedione in MeOH in the presence of Et_3N afforded 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-D-glucose (**6**) in yields >75%. Glycosidation of **6** with different alcohols (MeOH, CH_2=CH–CH_2OH, BnOH) under the Fischer conditions afforded mixtures of the corresponding alkyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)-amino]-α,β-D-glucopyranoside and -α-D-glucofuranoside. Removal of the *N*-protecting group gave high yields of the free aminodeoxyglyco-pyranosides and -furanosides. In addition to other known glycosides, allyl and benzyl 2-amino-2-deoxy-α-D-glucopyranoside and ethyl and allyl 2-amino-2-deoxy-α-D-glucofuranoside were obtained. An X-ray crystallographic study of **6** indicated that, in the solid state, it has the α-D configuration and that the pyranoside ring adopts the $^4C_1$ conformation.

INTRODUCTION

We have reported[1,2] on the utility of the 2,2-dimethoxy- and 2,2-diethoxycarbonylvinyl groups for protecting the amino function of amino sugars during Fischer glycosidation. For example, using derivatives **1** and **2**, methyl and ethyl

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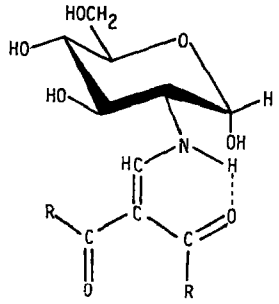


1 R = OMe

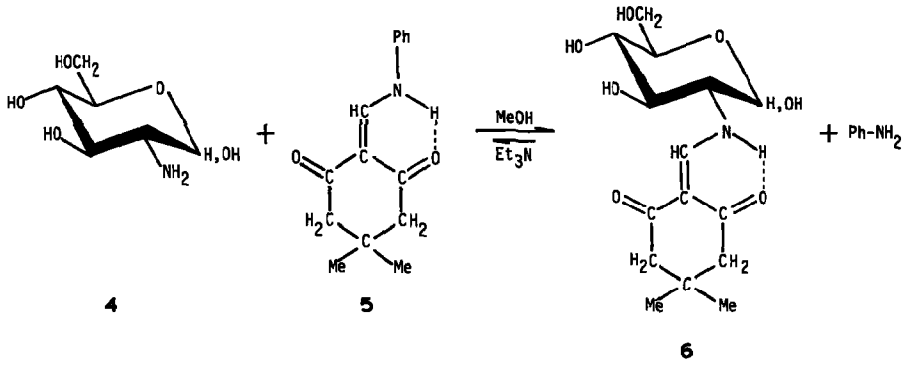
2 R = OEt

3 R = Me

2-amino-2-deoxy-α,β-D-glucopyranosides can be obtained easily in high yields, as can the rather inaccessible methyl 2-amino-2-deoxy-α-D-glucofuranoside. These *N*-protecting groups can be removed easily under mild, non-acidic conditions. However, the glycosidation reaction is accompanied by a transesterification process, and, when using alcohols other than MeOH and EtOH, complex mixtures are produced. In order to overcome this limitation, the *N*-(2,2-diacetylvinyl) derivative **3** was studied, but was found not to be a good substrate for glycosidation[2]. The different behaviour was associated with the degree of polarisation inside the 2,2-diacylvinylamino system; the amino function of the practically planar[3] and highly delocalised 2,2-diacetylvinylamino group of **3** bears a high positive charge which effectively inhibits the acid-catalysed glycosidation. The effect is not so pronounced in the less planar[4] and delocalised *N*-(2,2-dialkoxycarbonylvinyl) derivatives. We now report on the use of the 4,4-dimethyl-2,6-dioxocyclohexylidenemethyl group, which allows the 2-amino-2-deoxy-α,β-D-glucopyranosides and -α-D-glucofuranosides of the common alcohols to be obtained easily, although in modest yields. An X-ray crystallographic study of 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucopyranose (**6**) has been performed in order to better understand the relationship between the reactivity and conformation of these compounds.

RESULTS AND DISCUSSION

Preparation of [(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]glycoses. — Derivative **6** was obtained (>75% after recrystallisation) by reaction of 2-amino-2-deoxy-D-glucose hydrochloride (**4**) with the readily available[5] 5,5-dimethyl-2-phenylaminomethylene-1,3-cyclohexanedione (**5**) in MeOH-Et_3N. This is a reversible transamination process which could also be applied to prepare the

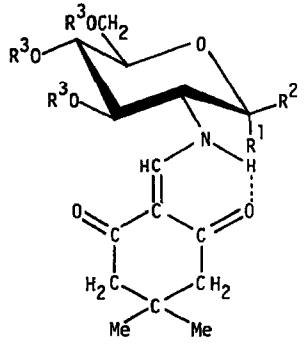


known[2] 2,2-diacetylvinyl derivative **3** (from phenylaminomethyleneacetylacetone[5]; 76%). The position of the equilibrium is determined by the p*K* values of the amino sugar (or other amines used in model reactions[6]) and aniline, being displaced in the direction of the aminoenedione of the more basic amine (in the above cases, **3** and **6**). Similarly, glycosides **8α** and **8β**, which were expected to be products of the methyl glycosidation of **6** described below, were unequivocally synthesised (97% and 87% yield, respectively) from methyl 2-amino-2-deoxy-α- or -β-D-gluco-pyranoside hydrochloride and **5**. Acetylation of **6**, **8α**, and **8β** afforded high yields of the corresponding acetates **7**, **9α**, and **9β**.

The analytical and spectral data (Tables I and II) of **6** and **7–9** were consistent with their assigned structures. These compounds had u.v. and i.r. absorptions very similar to those of simple, intramolecularly bonded 2-alkylaminomethylene-5,5-dimethyl-1,3-cyclohexanediones[6,7], and their ^{1}H-n.m.r. spectra indicated the pyranose ring structure and the anomeric configurations assigned. In contrast with what has been observed[2] with other *N*-acylvinyl derivatives of 2-amino-2-deoxy-D-glucose, the ^{1}H-n.m.r. spectrum of **6** in $(CD_3)_2SO$ showed that, under these conditions, this compound exists as a mixture of the α and β anomers in the ratio ~3:2; its acetylation afforded exclusively the α-tetra-acetate **7**. An X-ray crystallographic study (see below) of **6** confirmed the structure and conformation assigned, and showed that, in the solid state, it has the α-D configuration. As no mutarotation was observed in solution, it follows that the equilibrium **6α** ⇌ **6β** is reached too fast to be followed polarimetrically.

Fischer reactions. — The glycosidation reactions of **6** were much slower than those[2] of the analogous *N*-(2,2-dialkoxycarbonylvinyl) derivatives, and the longer reaction times required resulted in hydrolytic side-reactions and lower yields of products. The reactions had to be stopped before all of the starting **6** had been consumed.

With boiling, methanolic 1.25% hydrogen chloride, **6** gave (t.l.c.) **8α**, its β anomer (**8β**), and methyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidene-methyl)amino]-α-D-glucofuranoside (**14**). After 7 h, **6** was still present, and column



7 R^1= OAc, R^2= H, R^3= Ac

8α R^1= OMe, R^2= R^3= H

8β R^1= R^3= H, R^2= OMe

9α R^1= OMe, R^2= H, R^3= Ac

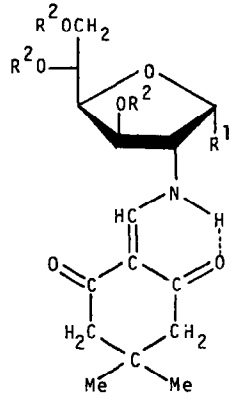
9β R^1= H, R^2= OMe, R^3= Ac

10 R^1= OAll, R^2= R^3= H

11 R^1= OAll, R^2= H, R^3= Ac

12 R^1= OBn, R^2= R^3= H

13 R^1= OBn, R^2= H, R^3= Ac



14 R^1= OMe, R^2= H

15 R^1= OMe, R^2= Ac

16 R^1= OAll, R^2= H

17 R^1= OAll, R^2= Ac

chromatography afforded **8α** + **8β** (20%), having the same mobility, and **14** (16%). The ^{1}H-n.m.r. spectrum and the $[\alpha]_D$ value for **8α** + **8β** indicated an αβ-ratio of ~7:3. Acetylation of **8α** + **8β**, and fractional crystallisation of the mixture of acetates obtained, afforded **9α** (58%) and **9β** (29%). When longer reaction times and lower temperatures were used, the proportion of **14** was higher, but the overall yield of glycosides was lower. After 7 days at room temperature, **14** (8%) was practically the only product.

Glycosidation of **6** with allyl alcohol containing 2% of hydrogen chloride was faster, giving, after 3 h and column chromatography, allyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucopyranoside (**10**) (25%) and the α-D-furanoside **16** (10%). The similar reaction with benzyl alcohol was very slow; in the first stages of the reaction, the glycoside **12** and a second product, presumably the corresponding benzyl α-furanoside, were detected. After 40 h, the main product was **12** (>30% after column chromatography).

Acetylation of **10, 12, 14,** and **16** afforded the corresponding tri-acetates **11, 13, 15,** and **17**. The analytical and spectral properties (Tables I and II) of these products were in agreement with the assigned structures. The analytical periodate

TABLE I

U.V. AND I.R. ABSORPTIONS FOR COMPOUNDS **6–17**

Compound	λ_{max}, *nm (log ε)*[a]	*ν (cm⁻¹)*[b]			
		N–H	*C=O*		*C=C–NH*[c]
6	302 (4.25)[d] 252 (4.05)	[e]	1670vs	1605vs	1585vssh
7	306 (4.08)[f] 252 (3.63)	3190w	1670s	1610vs	1580s
8α	303 (4.31) 249 (4.17)	[e]	1660s	1600vs	1585vs
8β	301 (4.30) 251 (4.15)	[e]	1660vs	1600vs	1580vs
9α	306 (4.23)[f] 247 (4.13)	3190w	1670vs	1600vs	1580ssh
9β	306 (4.25)[f] 245 (4.17)	3190w	1670vs	1600vs	1580vs
10	302 (4.33) 247 (4.23)	[e]	1665s	1600s	1595s
11	303 (4.20)[f] 247 (4.12)	[g]	1670s	1610vs	1580s
12	304 (4.25) 249 (4.13)	[e]	1670s	1605vs	1575s
13	304 (4.22) 244 (4.07)	3190w	1670s	1600vs	1570s
14	305 (4.36) 248 (4.25)	[e]	1660s	1600vs	1580s
15	305 (4.30) 247 (4.21)	3190w	1665vs	1600vs	1580ssh
16	305 (4.36) 248 (4.25)	[e]	1660s	1595vs	1580s
17	307 (4.25)[f] 247 (4.14)	[g]	1670vs	1615vs	1575s

[a]In EtOH unless otherwise indicated. [b]In KBr. [c]Assigned to a mixed ν(C=C) + δ(N–H) mode. [d]In H_2O. [e]Obscured by the ν(O–H) absorption. [f]In $CHCl_3$. [g]None observed.

oxidation of **10** required 1 mol of oxidant and did not produce either formic acid or formaldehyde; the furanoside **16** consumed 1 mol of periodate and liberated 1 mol of formaldehyde, but not formic acid. The α-D configuration of **14** was demonstrated by its transformation into methyl 2-amino-2-deoxy-α-D-gluco-furanoside (**26**) and into **18** (ref. 2) (see below). The other furanosides **15–17**, and **21**, had $[\alpha]_D$ and $J_{1,2}$ values similar to those of **14**, thus indicating that each has the α-D configuration.

Removal of the *N*-protecting group was best accomplished by hydrolysis of the sugar aminoenedione in water–acetone in the presence of Amberlite IRA-400 (HO^-) resin at room temperature[2]. The reaction was complete in some few minutes, and the aminoglycoside was the only product in the supernatant solution.

TABLE II

^{1}H-N.M.R. DATA[a] (δ, p.p.m.) FOR COMPOUNDS **6–17**

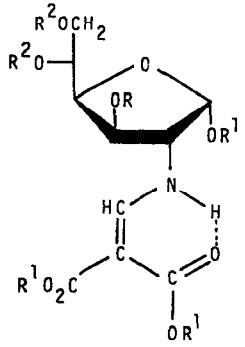
Compound	*NH*	*=CH*	*CMe_2*	*CH_2*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*1-OR*	*OAc*
6[b]	10.85dd	7.95d	0.95s	2.33s 2.40s	5.07d 4.67d	←		3.10–3.55m			→		
7[c]	10.99dd	8.02d	1.03s	2.33s 2.35s	6.27d	3.72ddd	5.39t	5.15t	4.08ddd	4.35dd	4.12dd		1.99s 2.04s 2.09s 2.29s
8α[b]	10.90dd	8.04d	0.98s 0.99s	2.27s 2.33s	4.83d	←		3.05–3.72m			→	3.40s	
8β[b]	10.80dd	7.95d	0.96s	2.24s 2.30s	4.57d	3.14ddd	3.53t	3.17t	3.29m	3.74dd	3.51dd	3.37s	
9α[c]	10.83dd	7.94d	0.97s	2.26s 2.30s	4.84d	3.46ddd	5.27t	4.98t	3.97ddd	4.25dd	4.04dd	3.44s	1.90s 1.96s 2.04s
9β[c]	11.06dd	8.04d	1.04s 1.05s	2.34s 2.38s	4.41d	3.35ddd	5.25m	5.09m	3.73ddd	4.34dd	4.15dd	3.51s	2.01s 2.04s 2.11s
10[b]	10.80dd	8.05d	0.94s	2.22s 2.30s	4.92d	3.25m	←	3.70–4.20m	→		3.40–3.70m	3.45m 5.20dt 5.30dt 6.00m	
11[c]	10.86dd	7.95d	0.97s	2.26s 2.31s	4.99d	3.49ddd	5.37t	4.99t	4.10m	4.32dd	4.10dd	4.20m 5.33m 5.97m	1.91s 1.96s 2.04s
12[b]	11.04dd	8.05d	0.97s	2.32s	4.98d	3.32ddd	←	3.54–3.79m			→	4.51d 4.74d 7.37m	
13[c]	10.92dd	7.90d	1.90s 1.94s	2.33s 2.56s	4.96d	4.46ddd	5.31t	4.99t	3.98ddd	4.22dd	3.93dd	4.60d 4.72d 7.42m	1.90s 1.94s 2.04s
14[b]	11.02dd	8.11d	0.98s	2.27s 2.32s	5.01d	4.07dt	4.23t	3.95t	3.73ddd	3.60dd	3.43dd	3.33s	

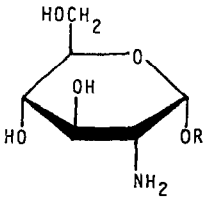
15[c]	11.26d	8.12d	1.04s 1.06s	2.35s 2.38s	5.11d	3.95ddd	5.34m	4.41m	5.28ddd	4.54dd	4.16dd	3.47s	2.01s 2.02s 2.08s
16[b]	11.11dd	8.13d	0.96s 0.97s	2.25s 2.30s	5.14d	4.11ddd	4.31t	3.98t	3.84ddd	3.63dd	3.47dd	4.00m 5.15dc 5.35dc 5.89m	
17[c]	11.26dd	8.13d	1.05s 1.06s	2.35s 2.39s	5.28d	3.99m	5.26t	4.46t	5.35m	4.54dd	4.16dd	4.12m 5.37m 5.92m	2.02s 2.08s 2.09s

COUPLING CONSTANTS (Hz)

	$J_{NH,=CH}$	$J_{NH,2}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
6	13.8	10.1	3.0[d] 7.9[e]						
7	13.8	10.2	3.5	10.0	9.9	9.9	4.0	2.2	−12.4
8α	14.1		2.8						
8β	14.1	8.9	8.2	10.0	9.9	8.9	7.7	1.4	−11.1
9α	13.7	9.8	3.5	9.9	9.9	9.9	4.4	2.1	−12.3
9β	13.2	8.4	7.9	9.4		9.4	4.5	2.5	−12.4
10	14.0	9.0	3						
11	13.7	9.5	3.8	9.9	9.8	9.7	4.8	1.3	−12.8
12	14.0	8.6	2.9						
13	13.5	10.0	3.8	10.0	10.0	10.0	4.6	2.3	−12.8
14	14.1	4.8	4.8	5.7	6.5	6.5	3.8	6.3	−11.1
15	14.5	8.7	5.1	4.4	5.6	8.7	2.3	5.6	−12.1
16	14.1	5.5	4.8	6.3	6.3	6.3	3.6	6.3	−11.4
17	13.7	8.7	5.1	3.9	5.4	9.5	2.5	5.0	−12.2

[a]At 200 MHz. [b]In $(CD_3)_2SO$. [c]In $CDCl_3$. [d]Of the α anomer. [e]Of the β anomer.





18 R^1 = Me, R^2 = H

19 R^1 = Me, R^2 = Ac

20 R^1 = Et, R^2 = H

21 R^1 = Et, R^2 = Ac

22 R = Me

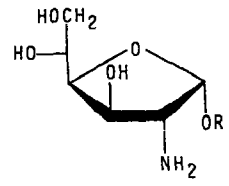
23 R = Et

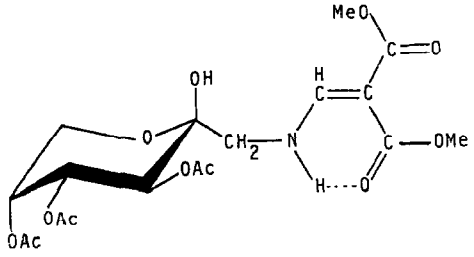
24 R = All

25 R = Bn

Ethyl 2-amino-2-deoxy-α-D-gluco-pyranoside (**23**) and -furanoside (**27**) were better obtained from **2**; treatment of this compound with boiling EtOH in the presence of Amberlyst-15 resin gave ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside[2] and **20** (15%). *N*-Deprotection then afforded **23** and **27**, respectively; the former compound, previously described[2] as a syrup, was obtained crystalline. The new allyl (**24**) and benzyl (**25**) 2-amino-2-deoxy-α-D-glucopyranosides were also crystalline. The new ethyl (**27**) and allyl (**28**) 2-amino-2-deoxy-α-D-gluco-furanosides were syrups; **28** was characterised as its *N*-acetyl derivative.

The above and previous[2] results indicate that the 2,2-dimethoxy- and 2,2-diethoxy-carbonylvinyl groups can be used conveniently to prepare methyl and ethyl 2-amino-2-deoxy-α-D-glucopyranosides in fairly good yields (~50% from **4**),





26 R = Me

27 R = Et

28 R = All

29

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR 6[a]

C-1–C-2	1.526	N-1–C-21	1.471
C-1–C-6	1.536	O-1–C-11	1.417
C-1–C-12	1.535	O-1–C-51	1.443
C-1–C-13	1.525	C-11–O-11	1.400
C-2–C-3	1.474	C-11–C-21	1.516
C-3–C-4	1.443	C-21–C-31	1.523
C-3–O-13	1.269	C-31–O-31	1.448
C-4–C-5	1.437	C-31–C-41	1.520
C-4–C-7	1.408	C-41–O-41	1.437
C-5–C-6	1.509	C-41–C-51	1.537
C-5–O-15	1.262	C-51–C-61	1.535
C-7–N-1	1.315	C-61–O-61	1.421
C-12–C-1–C-13	108.8	C-7–N-1–C-21	123.5
C-6–C-1–C-13	112.4	C-11–O-1–C-51	113.3
C-6–C-1–C-12	108.6	O-1–C-11–C-21	109.7
C-2–C-1–C-13	110.1	O-1–C-11–O-11	112.1
C-2–C-1–C-12	110.2	O-11–C-11–C-21	108.2
C-2–C-1–C-6	106.5	N-1–C-21–C-11	108.2
C-1–C-2–C-3	114.0	C-11–C-21–C-31	111.1
C-2–C-3–O-13	119.9	N-1–C-21–C-31	110.4
C-2–C-3–C-4	119.1	C-21–C-31–C-41	108.7
C-4–C-3–O-13	120.8	C-21–C-31–O-31	108.6
C-3–C-4–C-7	118.4	O-31–C-31–C-41	109.1
C-3–C-4–C-5	119.0	C-31–C-41–C-51	108.7
C-5–C-4–C-7	122.3	C-31–C-41–O-41	107.9
C-4–C-5–O-15	120.7	O-41–C-41–C-51	107.4
C-4–C-5–C-6	120.6	O-1–C-51–C-41	109.7
C-6–C-5–O-15	118.6	C-41–C-51–C-61	113.1
C-1–C-6–C-5	113.0	O-1–C-51–C-61	105.5
C-4–C-7–N-1	123.3	C-51–C-61–O-61	111.0

[a]Mean e.s.d.s, 0.015 Å and 0.9°.

and also the correspnding α-furanosides (10–15% from **4**). The 4,4-dimethyl-2,6-dioxocyclohexylidenemethyl group gives lower yields of both allyl and benzyl α-glyco-pyranosides and -furanosides. The *N*-protecting group can be removed under mild, non-acidic conditions, and the free aminoglycosides are easily obtained. No other general procedure for the preparation of alkyl 2-amino-2-deoxy-α-D-gluco-furanosides seems to be available.

X-Ray structure of **6**. — The positional and isotropic thermal parameters have been deposited*. The bond lengths and angles are listed in Table III. Fig. 1 shows a view of the molecule projected on the plane *ac* with the crystallographic numbering used. The results clearly indicate the existence of extensive electron delocalisa-

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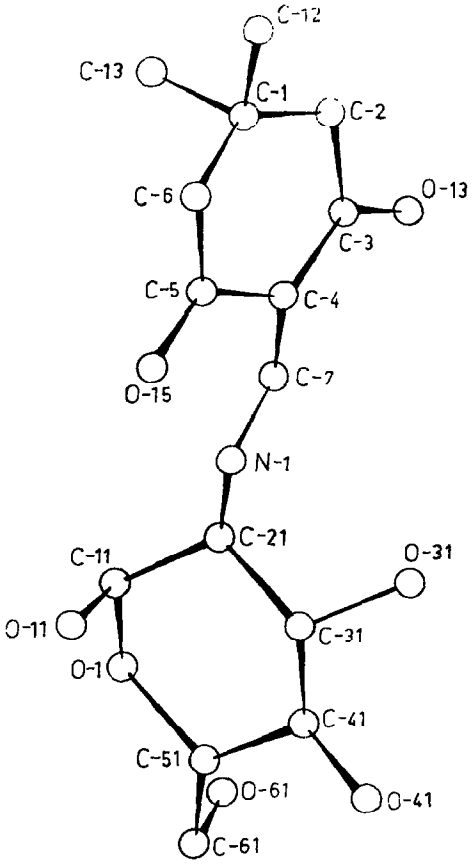

Fig. 1. A projection of the molecule of **6** on the plane *ac* with the crystallographic numbering used.

tion involving the donor N-1 and the two acceptor carbonyl groups C-3–O-13 and C-5–O-15. The C-4–C-7 bond distance (1.408 Å) is significantly longer than a formal C=C bond[8] (1.336 Å) and there is a corresponding shortening of the N-1–C-7 bond (1.315 Å) which is shorter than the 1.452 Å reported[9] for an N–C(sp^2) bond. On the acceptor side, the C-4–C-5 and C-3–C-4 bonds are 1.437 Å and 1.443 Å, which are also shorter than the 1.487 Å value reported[10] for a C(sp^2)–C(sp^2) single-bond. The system N-1–C-7–C-4 $\begin{matrix}\diagup\text{C-5–O-15}\\ \diagdown\text{C-3–C-13}\end{matrix}$ is approximately planar (maximum deviation from the best square plane, 0.073 Å), and C-2 and C-6 are nearly in the same plane (maximum deviation, 0.182 Å), which agrees well with the half-boat conformation found for the cyclohexane ring. Cremer and Pople's puckering parameters[11] for the sequence C-1–C-2–C-3–C-4–C-5–C-6 are Q 0.50 Å, ϕ −174°, and θ 125°, and Nardelli asymmetry parameters[12] are ΔC_s(C-1) = 0.032 and ΔC_2(C-2–C-1) = 0.090°. The torsion angles around the C-4–C-7 double-bond are 179° and

−5°, the distortion probably being due to the hydrogen bond between N-1 and O-15. The pyranose ring adopts the $^4C_1$(D) conformation with O-11 axial, and the C–C, C-11–O-1, and C-51–O-1 distances are in good agreement with those observed[3,13] for related structures. Crystal packing consists of a three-dimensional network of molecules linked by O–H · · · O bonds, [O-31 · · · O-112 ($-x,y$ + 1/2, $-z$ + 1) = 2.847; O-61 · · · O-112 (x,y + 1, z) = 2.954; O-111 · · · O-112 ($-x,y$ − 1/2, $-z$ + 1) = 2.765; O-61 · · · O-11 (x,y + 1, z) = 3.041; and O-41 · · · O-61 ($-x,y$ − 1/2, $-z$ + 1) = 3.018 Å]. There is one intramolecular hydrogen-bond N-1 · · · O-15 = 2.646 Å, showing a chelated structure.

Comparing the results for compound **6** with those obtained[3] for **3**, it can be seen that the electron delocalisation and, consequently, the positive charge accumulated on the amino function of both molecules do not differ significantly. On the other hand, the X-ray crystallographic analysis[4] of the related compound **29** (ref. 1) indicates that, in this structure, the chelated carbonylvinylamino group is planar, whereas the free methoxycarbonyl group, which adopts the *s-trans* disposition, is tilted by 25° from the plane of the chelate and is not strongly conjugated. The 2,2-dimethoxycarbonylvinyl group is less delocalised, and the NH bears a lesser positive charge. In addition, the results of the glycosidation reactions discussed above and those previously reported[2] indicate that the 2,2-dimethoxycarbonylvinyl group is a better protecting group than those in **3** and **6**. This supports the view[2] that the polarisation inside the 2,2-diacylvinylamino group is a factor controlling the Fischer glycosidation. However, the fact that **3** and **6**, each having a highly polarised *N*-protecting group, behave differently under the glycosidation conditions suggests that other factors may also operate.

EXPERIMENTAL

General methods. — Unless stated otherwise, these were as described previously[2]. N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si), unless otherwise specified, using a Varian XL-90 or XL-200 spectrometer. All reactions were monitored by t.l.c. Acetates were prepared as described in ref. 2.

*2-Deoxy-2-[4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α,β-*D*-glucopyranose* (**6**). — A suspension of **4** (10.0 g, 46.0 mmol) and **5** (11.36 g, 46.0 mmol) in MeOH (225 mL) containing Et_3N (16 mL) was vigorously stirred at room temperature for 3 h. The resulting solution was concentrated until initial crystallisation and refrigerated. The solid was recrystallised from H_2O to give **6** (11.4 g, 75%), m.p. 225–227°, $[\alpha]^{25}_{5461}$ +94° (constant), $[\alpha]^{25}_{D}$ +72° (constant) (*c* 1, ethanol).

Anal. Calc. for $C_{15}H_{23}NO_7$: C, 54.70; H, 7.04; N, 4.25. Found: C, 54.52; H, 7.14; N, 4.44.

The tetra-acetate **7** (72%) had m.p. 173–174° (from EtOH), $[\alpha]^{25}_{5461}$ +130°, $[\alpha]^{25}_{D}$ +98° (*c* 1, chloroform). Spectral data for **6** and **7** are given in Tables I and II.

Anal. Calc. for $C_{23}H_{31}NO_{11}$: C, 55.53; H, 6.28; N, 2.81. Found: C, 55.65; H, 6.39; N, 2.79.

2-Deoxy-2-[(2,2-diacetylvinyl)amino]-α-D-glucopyranose (**3**). — Prepared from **4** and phenylaminomethyleneacetylacetone[5] as described above for **6**, with recrystallisation from EtOH, **3** (76%) had m.p. 203–205° and was identical with an authentic sample[2].

Methyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucopyranoside (**8α**). — Prepared from methyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride[14] and **5**, as described for compound **6**, **8α** (97%) had m.p. 241–243° (from EtOH), $[\alpha]_{5461}^{23}$ +143.5°, $[\alpha]_D^{25}$ +117° (*c* 1, ethanol).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.96; H, 7.34; N, 4.08. Found: C, 56.20; H, 7.68; N, 4.09.

The tri-acetate **9α** (97.6%) had m.p. 165–166° (from EtOH), $[\alpha]_{5461}^{25}$ +200° (*c* 1, dichloromethane). The spectral data for **8α** and **9α** are listed in Tables I and II.

Anal. Calc. for $C_{22}H_{31}NO_{10}$: C, 56.28; H, 6.65; N, 2.98. Found: C, 56.48; H, 6.90; N, 3.12.

Methyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-β-D-glucopyranoside (**8β**). — Prepared from methyl 2-amino-2-deoxy-β-D-glucopyranoside hydrochloride[15] and **5**, as described for **6**, **8β** (87%) had m.p. 199–201° (from EtOH), $[\alpha]_{5461}^{23}$ 0°, $[\alpha]_D^{23}$ 0° (*c* 1, ethanol).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.96; H, 7.38; N, 4.08. Found: C, 55.75; H, 7.39; N, 4.15.

The tri-acetate **9β** (99.3%) had m.p. 151–152° (from EtOH), $[\alpha]_{5461}^{25}$ +61° (*c* 1, dichloromethane). Spectral data for **8β** and **9β** are listed in Tables I and II.

Anal. Calc. for $C_{22}H_{31}NO_{10}$: C, 56.28; H, 6.65; N, 2.98. Found: C, 56.02; H, 6.80; N, 2.78.

Glycosidation of **6**. — (*a*) A solution of **6** (2.0 g, 6.1 mmol) in MeOH (100 mL) containing 1.25% of HCl was boiled under reflux for 7 h. T.l.c. ($CHCl_3$–MeOH, 7:1) then indicated the presence of **8α** + **8β** (R_F 0.42, major product), **14** (R_F 0.48), **6** (R_F 0.15, traces), and decomposition products (R_F ~1 and ~0). The solution was stirred with lead carbonate (2.0 g), filtered, and concentrated to ~1/3 volume. Compound **6** was removed, the filtrate was concentrated to a syrupy mixture (1.63 g, 78.4%) of **8α** + **8β** and **14** (t.l.c.). Column chromatography ($CHCl_3$–MeOH, 95:5) of this material afforded, first, methyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucofuranoside (**14**; 0.33 g, 16%), isolated as a foam, $[\alpha]_{5461}^{25}$ +189°, $[\alpha]_D^{25}$ +158° (*c* 1, ethanol).

Anal. Calc. for $C_{16}H_{25}NO_7 \cdot 1.5\ H_2O$: C, 51.88; H, 7.62; N, 3.78. Found: C, 51.69; H, 7.16; N, 3.99.

The tri-acetate **15** (69%) had m.p. 113–115° (from EtOH), $[\alpha]_{5461}^{23}$ +151° (*c* 0.8, dichloromethane). The spectral data for **14** and **15** are listed in Tables I and II.

Anal. Calc. for $C_{22}H_{31}NO_{10}$: C, 56.28; H, 6.65; N, 2.98. Found: C, 56.13; H, 6.93; N, 2.67.

Eluted second was a crystalline mixture (0.38 g, 18.3%) of **8α** and **8β**, m.p. 135–137° (from EtOH), $[\alpha]_{5461}^{23}$ +93°, $[\alpha]_D^{23}$ +75° (*c* 1, ethanol).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.96; H, 7.34; N, 4.08. Found: C, 56.15; H, 7.40; N, 4.15.

Acetylation of **8α** + **8β** yielded a crystalline mixture (100%) of **9α** (R_F 0.50; Et_2O) and **9β** (R_F 0.40). Crystallisation from EtOH afforded **9α** (0.32 g, 58.4%), m.p. 165–166°. Concentration of the mother liquor and recrystallisation of the residue gave **9β** (0.16 g, 29%), m.p. 151–152°.

When a solution of **6** (3.0 g) in MeOH (60 mL) containing 1.25% of HCl was stored at room temperature for 7 days, the main product was **14** (t.l.c.). Work-up as described above gave **14** (0.25 g, 8%).

(*b*) A solution of **6** (4.0 g, 12.0 mmol) in allyl alcohol (100 mL) containing 2% of HCl was boiled under reflux for 3 h. T.l.c. ($CHCl_3$–MeOH, 7:1) then indicated the presence of **16** (R_F 0.46), **10** (R_F 0.39), **6** (R_F 0.20), and products having R_F ~1 and ~0.

Concentration of the reaction mixture gave crystalline **4** (0.78 g, R_F 0). Concentration of the mother liquor afforded a syrup (3.1 g), column chromatography ($CHCl_3$ and then $CHCl_3$–MeOH, 95:5) of which afforded, first, allyl 2-deoxy-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucofuranoside (**16**; 0.45 g, 10%), m.p. 125–127°, $[\alpha]^{22}_{5461}$ +217.5°, $[\alpha]^{22}_{D}$ +160° (*c* 1, chloroform).

Anal. Calc. for $C_{18}H_{27}NO_7$: C, 58.52; H, 7.37; N, 3.79. Found: C, 58.42; H, 7.40; N, 3.53.

Compound **16** consumed[16] (in 15 min) 1.0 mol of metaperiodate, and liberated 0.95 mol of formaldehyde.

The tri-acetate **17** (82%) had m.p. 126–128° (from EtOH–H_2O, 1:2), $[\alpha]^{22}_{5461}$ +135°, $[\alpha]^{22}_{D}$ +112° (*c* 1, chloroform). The spectral data for **16** and **17** are listed in Tables I and II.

Anal. Calc. for $C_{24}H_{33}NO_{10}$: C, 58.17; H, 6.71; N, 2.83. Found: C, 58.24; H, 6.73; N, 2.79.

Eluted second was a mixture (0.14 g, 3.21%) of **10** and **16**, and eluted third was allyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucopyranoside (**10**; 1.1 g, 24%), m.p. 210–212°, $[\alpha]^{22}_{5461}$ +156°, $[\alpha]^{22}_{D}$ +142° (*c* 0.66, chloroform).

Anal. Calc. for $C_{18}H_{27}NO_7$: C, 58.52; H, 7.37; N, 3.79. Found: C, 58.46; H, 7.63; N, 3.90.

Compound **10** consumed[16] (in 45 min) 1.0 mol of metaperiodate and did not produce formaldehyde.

The tri-acetate **11** (74.6%) had m.p. 122–124° (from EtOH), $[\alpha]^{22}_{5461}$ +175°, $[\alpha]^{22}_{D}$ +144° (*c* 0.85, chloroform). The spectral data for **10** and **11** are listed in Tables I and II.

Anal. Calc. for $C_{24}H_{33}NO_{10}$: C, 58.17; H, 6.71; N, 2.83. Found: C, 58.33; H, 6.67; N, 2.54.

(*c*) A suspension of **6** (4.0 g, 12.0 mmol) in benzyl alcohol (100 mL) containing 2.5 g of HCl and molecular sieves (3 Å) was heated at 100–110°. After ~3 h, t.l.c. ($CHCl_3$–MeOH, 6:1) revealed a product with R_F 0.60, **12** (R_F 0.56), and **6** (R_F 0.15).

After 37 h, **12** was the only product. Work-up in the usual way and column chromatography afforded benzyl 2-deoxy-2-[(4,4-dimethyl-2,6-dioxocyclohexylidenemethyl)amino]-α-D-glucopyranoside (**12**; 1.43 g, 28.6%), m.p. 228–229° (from MeOH), $[\alpha]_D^{22}$ +122.5° (*c* 1, methanol).

Anal. Calc. for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.96; N, 3.34. Found: C, 62.78; H, 7.14; N, 3.20.

The tri-acetate **13** (91%) had m.p. 168–169° (from EtOH), $[\alpha]_D^{22}$ +109° (*c* 1, chloroform). The spectral data for **12** and **13** are listed in Tables I and II.

Anal. Calc. for $C_{28}H_{35}NO_{10}$: C, 61.64; H, 6.46; N, 2.56. Found: C, 61.38; H, 6.53; N, 2.42.

Ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucofuranoside (**20**). — A stirred solution of **2** (4.0 g, 12 mmol) in EtOH (200 mL) was boiled for 24 h under reflux with Amberlyst-15 (H^+) resin (32.0 g). The resin was filtered-off and rinsed well with EtOH. The combined filtrate and washings were concentrated to yield a mixture (3.80 g) of **20** (R_F 0.58; t.l.c., $CHCl_3$–EtOH, 9:1), ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α- (R_F 0.50) and -β-D-glucopyranoside (R_F 0.45), and **2** (R_F 0.20). Column chromatography ($CHCl_3$ and then $CHCl_3$–EtOH, 8:2) afforded, first, **20** (0.63 g, 15%), m.p. 96–98° (from EtOH); $[\alpha]_D^{29}$ +112° (*c* 1, ethanol); $\lambda_{max}^{H_2O}$ 223 and 279 nm (log ε 4.14 and 4.43); ν_{max}^{KBr} 3470s, 3370m and 3180w (OH, NH), 1695s, 1680vs, 1670vs and 1645m (C=O), and 1600 cm^{-1} (C=C–NH).

Anal. Calc. for $C_{16}H_{27}NO_9$: C, 50.92; H, 7.21; N, 3.71. Found: C, 50.80; H, 7.24; N, 3.50.

Compound **20** consumed[16] 1.0 mol of metaperiodate and liberated 0.95 mol of formaldehyde.

The tri-acetate **21** (100%) was a syrup, $[\alpha]_D^{18}$ +125° (*c* 0.88, tetrachloromethane); λ_{max}^{EtOH} 220 and 278 nm (log ε 4.15 and 4.40); $\nu_{max}^{CCl_4}$ 3260w (NH), 1718m, 1690s, and 1655s (C=O), 1600s cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (200 MHz, $CDCl_3$): δ 9.30 (dd, 1 H, $J_{NH,=CH}$ 14.0, $J_{NH,2}$ 8.2 Hz, NH), 8.05 (d, 1 H, =CH), 5.29 (dd, 1 H, $J_{2,3}$ 3.9, $J_{3,4}$ 5.5 Hz, H-3), 5.25 (ddd, 1 H, $J_{4,5}$ 8.6, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.4 Hz, H-5), 5.19 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 4.54 (dd, 1 H, $J_{6,6'}$ −12.2 Hz, H-6), 4.41 (dd, 1 H, H-4), 4.25 (q, 2 H, *J* 7.0 Hz, CO_2Et), 4.19 (q, 2 H, *J* 7.0 Hz, CO_2Et), 4.13 (dd, 1 H, H-6'), 3.90 (ddd, 1 H, H-2), 3.83 (dq, 1 H, *J* 8.9 and −14.4 Hz, OCH_2CH_3), 3.60 (dq, 1 H, OCH_2CH_3), 2.08, 2.07, 2.02 (3 s, each 3 H, 3 AcO), 1.33 (t, 3 H, OCH_2CH_3), 1.28 (t, 3 H, CO_2Et), and 1.27 (s, 3 H, CO_2Et).

Anal. Calc. for $C_{22}H_{33}NO_{12}$: C, 52.48; H, 6.60; N, 2.78. Found: C, 52.74; H, 6.65; N, 2.69.

Eluted second was ethyl 2-deoxy-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside (1.26 g, 29.3%), m.p. 114–115° (from AcOEt) (lit.[2] m.p. 114–117°).

Eluted third was ethyl 2-deoxy-[(2,2-diethoxycarbonylvinyl)amino]-β-D-glucopyranoside (1.56 g, 36%), isolated as a syrup. Its tri-acetate (72%) had m.p. 114–116°, $[\alpha]_D^{18}$ +17° (*c* 0.8, dichloromethane); λ_{max}^{EtOH} 217 and 276 nm (log ε 4.10 and 4.35); ν_{max}^{KBr} 3250w (NH), 1755vs (AcO), 1690s and 1645s (C=O), and 1603s

cm^{-1} (C=C–NH). ^{1}H-N.m.r. data (200 MHz, $CDCl_3$): δ 9.10 (dd, 1 H, $J_{NH,=CH}$ 13.4, $J_{NH,2}$ 8.7 Hz, NH), 8.00 (d, 1 H, =CH), 5.20 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.02 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.42 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.32 (dd, 1 H, $J_{6,6'}$ −12.3 Hz, H-6), 4.30 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.25 (q, 2 H, *J* 7.0 Hz, CO_2Et), 4.18 (q, 2 H, *J* 7.0 Hz, CO_2Et), 4.13 (dd, 1 H, H-6'), 3.96 (dq, 1 H, *J* 8.9 and 14.4 Hz, OCH_2CH_3), 3.70 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 7.7, $J_{5,6'}$ 2.5 Hz, H-5), 3.56 (dq, 1 H, OCH_2CH_3), 2.10, 2.03, 2.02 (3 s, each 3 H, 3 AcO), 1.34 (t, 6 H, 2 OCH_2CH_3 of CO_2Et and/or OEt), and 1.28 (t, 3 H, OCH_2CH_3 of CO_2Et or OEt).

Anal. Calc. for $C_{22}H_{33}NO_{12}$: C, 52.48; H, 6.60; N, 2.78. Found: C, 52.20; H, 6.56; N, 2.66.

Removal of the N*-protecting group.* — The following experiment is typical. A solution of **8α** (0.10 g) in Me_2CO–H_2O (2:1, 10 mL) was stirred with Amberlite IRA-400 (HO^-) resin (12 mL) for 15 min at room temperature. The resin was filtered-off and rinsed well with Me_2CO–H_2O (2:1), and the combined filtrate and washings were concentrated to give methyl 2-amino-2-deoxy-α-D-glucopyranoside (**22**; 0.40 g, 71%), m.p. 154–156° (from EtOH), $[\alpha]^{22}_{5461}$ +191°, $[\alpha]^{22}_{D}$ +161° (*c* 1, water), identical with an authentic sample.

Hydrolysis of **14** (0.10 g), as indicated above, and freeze-drying of the resulting solution afforded methyl 2-amino-2-deoxy-α-D-glucofuranoside (**26**; 0.10 g, 92.5%), as a syrup, $[\alpha]^{23}_{5461}$ +120°, $[\alpha]^{23}_{D}$ +105°, $[\alpha]^{23}_{3650}$ +298° (*c* 1.3, water).

Treatment of **26** (0.16 g, 0.18 mmol) in H_2O (3 mL) with methyl 3-methoxy-2-methoxycarbonylacrylate (0.17 g, 1.0 mmol) for 5 h, with concentration of the reaction mixture, afforded **18** (0.13 g, 92%), m.p. 146–148° (from EtOH), $[\alpha]^{20}_{D}$ +161° (*c* 0.5, chloroform), identical to the product described[2].

Ethyl 2-amino-2-deoxy-α-D-glucopyranoside (**23**, 71%), obtained from ethyl 2-deoxy-2-[(2,2-diethoxycarbonylvinyl)amino]-α-D-glucopyranoside, had m.p. 137–138° (from EtOH), $[\alpha]^{29}_{D}$ +155° (*c* 1, ethanol).

Anal. Calc. for $C_8H_{17}NO_5$: C, 46.37; H, 8.27; N, 6.76. Found: C, 46.44; H, 8.46; N, 6.78.

The *N*-benzyloxycarbonyl derivative, prepared in the usual way[15], had m.p. 130–132° (from EtOH) and was identical to an authentic sample.

Ethyl 2-amino-2-deoxy-α-D-glucofuranoside (**27**, 90%), obtained from **18**, was a foam, $[\alpha]^{20}_{D}$ +101° (*c* 1.5, ethanol).

Anal. Calc. for $C_8H_{17}NO_5$: C, 46.37; H, 8.27; N, 6.76. Found: C, 46.41; H, 8.36; N, 6.53.

Allyl 2-amino-2-deoxy-α-D-glucopyranoside (**24**, 94.5%), prepared from **10**, had m.p. 117–118° (from EtOH), $[\alpha]^{25}_{5461}$ +176°, $[\alpha]^{25}_{D}$ +142.5° (*c* 0.8, water).

Anal. Calc. for $C_9H_{17}NO_5$: C, 49.30; H, 7.81; N, 6.39. Found: C, 49.30; H, 7.75; N, 6.21.

Allyl 2-amino-2-deoxy-α-D-glucofuranoside (**28**, 84.3%) was obtained from **16**, as a syrup, $[\alpha]^{18}_{D}$ +102° (*c* 1, water), R_{GlcN} 2.50 (p.c., BuOH–AcOH–H_2O, 4:1:1). Treatment of this product with Ac_2O in MeOH afforded the corresponding *N*-acetyl derivative, as an amorphous solid, R_F 0.59 (t.l.c.; $CHCl_3$–MeOH, 3:1), $[\alpha]^{18}_{D}$ +89.5° (*c* 0.8, ethanol).

Anal. Calc. for $C_{11}H_{19}NO_6$: C, 50.56; H, 7.33; N, 5.36. Found: C, 50.25; H, 7.33; N, 5.24.

Benzyl 2-amino-2-deoxy-α-D-glucopyranoside (**25**, 100%), obtained from **12**, had m.p. 141–143° (from Me_2CHOH), $[\alpha]_D^{25}$ +126° (*c* 0.5, ethanol).

Anal. Calc. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.75; H, 7.20; N, 5.45.

Treatment of **25** with Ac_2O in MeOH gave the corresponding *N*-acetyl derivative, m.p. 185–186°, $[\alpha]_D^{18}$ +166° (*c* 0.2, water); lit.[17], m.p. 185–186°, $[\alpha]_D^{20}$ +168° (water).

Crystal data for **6**. — The compound crystallised with two molecules of water, $C_{15}H_{23}NO_2 \cdot 2\ H_2O$, $M_r = 365$. Monoclinic, space group $P2_1$, $a = 12.974(2)$, $b = 5.751(1)$, $c = 12.639(2)$ Å; $\beta = 109.65(1)°$, $V = 888.1(2)$ Å, $Z = 2$, $D_c = D_m = 1.36$ g.cm^{-3}, μ(Mo$K\alpha$) = 0.105 mm^{-1}, $F(000) = 392$. Room temperature. Unit-cell parameters were obtained from the least-squares refinement of θ values of 25 reflections ($3 < \theta < 13$), using an Enraf–Nonius CAD-4 diffractometer. Mo$K\alpha$ radiation, $\lambda = 0.71069$ Å (graphite monochromator). A total of 2787 reflections were scanned ($-18 < h < 18$, $0 < k < 8$, $0 < l < 17$) and measured in the $2\theta < 60°$ range, $\omega - 2\theta$ mode. Two standard reflections ($60\bar{4}$ and $\bar{2}05$), monitored every 100 reflections, showed statistical fluctuations. 1332 observed reflections [$I > 2\sigma(Io)$] were used for the structure determination; corrections were made for Lorentz and polarisation factors; absorption and extinction were ignored. The structure was solved by direct methods using the MULTAN-80 programme[18]; 242 *E* values ($E > 1.70$) were used as input to Multan and the correct set with the highest figure of merit of 2.23 and the residual value of 19.23 gave approximate positions for 21 of the 27 non-H atoms; the remaining atoms were located from a Fourier synthesis. *F* was refined by full-matrix least squares. A difference Fourier synthesis up to $\sin\theta/\lambda = 0.45$ A^{-1} revealed the H atoms. Further refinement of *F* with non-H atoms isotropically produced convergence with $R = 0.09$, $R_w = 0.09$ ($w^{-1} = \sigma^2$), and $S = 1.93$. The thermal parameters assigned to H atoms were equal to those of bonded atoms. A final difference Fourier synthesis showed $\Delta\rho = \pm 0.35$ eÅ^{-3}. Maximum least-squares shift to error was 0.5. The XRAY-70 system[19] of computer programmes was used. Atomic scattering factors were obtained from ref. 20.

The rather high *R*-factor and e.s.d.s as well as the discrepancies between $|F_o|$ and $|F_c|$ seem to be due to extinction or absorption problems, resulting from the shape and mediocre quality of the crystals.

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