Tetrahedron Vol 49, No 43, pp 9759-9766, 1993
Printed in Great Britain

0040-4020/93 $6 00+00

SYNTHESIS AND SPECTROSCOPIC STUDIES OF ACETYLATED ALKYL 1-AZIDO-D-GLUCOPYRANOSIDES

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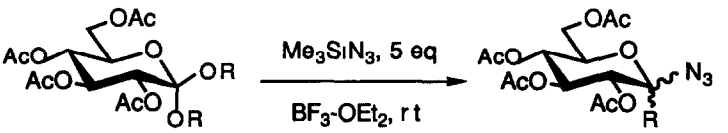
(*Received in Belgium* 4 *March* 1993, *accepted* 27 *July* 1993)

Abstract: On treatment with trimethylsilyl azide in the presence of boron trifluoride etherate, anomeric orthoesters undergo the exchange of one anomeric alkoxy group by an azido group to yield two epimeric mono azido derivatives (~85% total yield) It was observed that both lateral ^{15}N nuclei in axially oriented azido groups are shielded as compared to their equatorial counterparts

Our continuing interest in new synthetic pathways involving carbon-centered free radicals at the anomeric centre of sugar derivatives has recently highlighted unprecedented transformations of anomeric mono[1] and diazides[2-5] Such diazides are easily prepared either from peracetylated anomeric dihalides or perbenzylated δ-lactones[6] However, an alternative route towards these highly functionalised new compounds, using readily available anomeric orthoesters[7] appeared feasible In effect, mild procedures have been reported for the synthesis of mono[8] or diazido derivatives from carbonyl compounds[9,10] or chemically equivalent functionalities such as ketals[11] (including 2-methoxy-tetrahydropyran derivatives[12]), dithioketals[13] or orthoesters[14] In particular, a recent synthesis of the herbicidal natural product (+)-Hydantocidin[15], uses, in the crucial step, a Lewis acid-catalyzed opening of a spiroketal moiety in the presence of trimethylsilyl azide, to yield a mixture of anomeric azides These data, as well as the achievement of new synthetic transformations which take advantage of the versatility of the azido group, for the preparation of potentially active nitrogen-containing substances[5,16] prompted us to investigate the behaviour of sugar anomeric orthoesters when treated with trimethylsilyl azide in the presence of boron trifluoride etherate

Stirring a mixture of peracetylated anomeric orthoesters **1** or **2**, trimethylsilyl azide in excess (5eq) and BF_3-OEt_2 (1eq) at room temperature, in dry dichloromethane led to a clean and complete transformation of the starting materials Tlc monitoring of the reaction showed the gradual formation of two new compounds, slightly less polar than **1** or **2** After aqueous washings and workup, column chromatography allowed the purification of compounds **3** (63 %) and **4** (20 %) or **5** (64 %) and **6** (25 %) It is worth to note that under these conditions, the major isolated isomer displayed, in both cases, an equatorial azido group Use of acetonitrile instead of dichloromethane for the transformation of **1** did not change significantly the course of the reaction A partial transformation of **1** was observed when BF_3-OEt_2 was used in catalytic amounts, in both solvent[17] However, under these conditions, **4** was found more abundant than **3** by ^1H nmr analysis of



	R
1	Me
2	Et

	R	%
3	α-OMe	63
4	β-OMe	20
5	α-OEt	64
6	β-OEt	25

the reaction mixtures or preparative runs The ratio **4/3** was found as high as ~5/1 (Table 1) when only half of the starting material was transformed These conditions allowed efficient preparations of **4** which can be readily separated from the mixture of the starting material **1** and **3** by column chromatography Efforts to achieve the complete transformation of **1** with the same stereoselectivity failed (Table 1) as a result of the *in situ* anomerization of the kinetic product **4** in favour of the thermodynamically preferred anomer **3** As a matter of fact, stirring a pure sample of **4** in the presence of trimethylsilyl azide (5 eq) and BF_3-OEt_2 (1 eq) in CH_2Cl_2 for 70 mn resulted in a 70/30 mixture of **3** and **4** as shown by ^1H nmr More drastic conditions (larger amounts of BF_3-OEt_2 and/or trimethylsilyl azide, extended reaction times and/or heating) which were selected for achieving the substitution of the remaining alkoxy group in **3** and **4** by an azide anion, gave only disappointing results These experiments led, in our hands, either to extensive degradation of the products or to mixtures of the desired diazide **7** and remaining **3**, from which **7** could be isolated in modest yield (~25%)

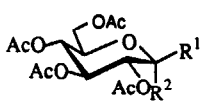
Table 1: Synthesis of **3** and **4** products distribution shown by ^1H nmr[a]

Solvent	BF_3-OEt_2 eq	Me_3SiN_3 eq	Reaction time	1	3	4
CH_2Cl_2	0 4	5	9 days	40	10	50
CH_2Cl_2	0 5	5	24 h	30	20	50
CH_2Cl_2	1	5	24 h	0	63[b]	20[b]
CH_3CN	0 4	5	5 days	16	27	57
CH_3CN	0 7	5	22 h	6	40	54
CH_3CN	1	5	19 h	0	55	45

a - Reaction mixtures contained only **3, 4** and eventually **1** The products distribution was calculated from the area of their methoxy singlets (deuteriochloroform solutions), b - isolated yields

Comparison of the ^1H or ^{13}C nmr spectra (Table 2) of derivatives **3-7** in order to assign the anomeric configuration of the azidoglucosides **3-6** was not conclusive In effect, the chemical shifts of H-2 and H-3 along the series were very similar (5 25 ±0 02 and 5 40 ±0 02 ppm) whereas a slight variation was observed for the H-5 resonances (3 90 ±0 01 ppm in **3** and **5**, 4 02 ppm in **4** and **6**) Since the H-3 signals were slightly shielded in structures **4** and **6** which showed simultaneously deshielded H-5 signals as compared to **3** and **5**, the chemical shifts of these nuclei were not equally affected by the axial substituent at the anomeric centre However, the aglycon methyl or methylene signals showed a 0 1 ppm difference in each anomeric

Table 2 ^{1}H, ^{13}C [a] and ^{15}N [b] nmr data of compounds **3 - 9**



	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	CH_3	CH_2		N-1	N-2	N-3
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$		J_{gem}	J_{vic}			
	C-1	C-2	C-3	C-4	C-5	C-6	C=O	CH_3	CH_2				
3		5 27	5 41	5 16	3 90	4 24	4 19	3 42			-290 3	-143 4	-159 0
		10 1	*9 5*	*9 9*	*4 2*	*2 5*	*12 2*						
	105 9	71 4[c]	71 0[c]	68 2[c]	70 4[c]	61 5		49 5					
4		5 26	5 40	5 10	4 02	4 24	4 13	3 52			-292 3	-143 1	-161 6
		9 9	*9 7*	*10 1*	*4 3*	*2 3*	*12 6*						
	106 9	71 6[d]	71 2[d]	67 7[d]	72 9[d]	61 2		51.2					
5		5 24	5 41	5 14	3 91	4 23	4 17	1 30	3 78	3 67			
		10 0	*9 7*	*10 0*	*4 6*	*2 4*	*12 4*		*9 8*	*7 1*			
	105 8	71 5[e]	71 1[e]	68 4[e]	70 4[e]	61 6		14 7	58 2				
6		5 26	5 38	5 10	4 02	4 22	4 12	1 24	3 88	3 79			
		9 9	*9 7*	*10 0*	*4 3*	*2 3*	*12 5*		*9 5*	*7 1*			
	106 9	71 7[d]	71 3[d]	67 8[d]	73 0[d]	61 3		15 0	60 0				
7[f]		5 23	5 37	5 16	4 17	4 28	4 18				-285 9	-143 6	-151 3
		9 9	*9 6*	*9 6*	*4 6*	*~2*	*12 7*				-289 6	-143 2	-154 9
	99 9	72 1[d]	70 8[d]	67 6[d]	72 1[d]	61 1							
8											-296 5	-138 4	-158.0
9											-301 0	-138 4	-164.4

[a] - The acetyl groups resonances are ^{1}H nmr δ **3** 2 00, 2 04, 2 11, 2 12, **4** . 2 01, 2 03, 2.09, 2.10, **5** 2.00, 2 04, 2 10, 2 11; **6** : 2.01, 2 03, 2.09, 2 10, **7** 2.01, 2 04, 2 11, 2 12, ^{13}C nmr δ **3** . 20 6, 20 7, 169 4, 169 6, 169.9, 170 6, **4** 20 3, 20.5, 20 5, 20 7, 169.0, 169.4, 170.0, 170 5, **5** . 20.5, 20 6, 169 4, 169 7, 169 9, 170 5, **6** 20 3, 20 6, 20 6, 20 7, 169 0, 169 4, 170 0, 170 5, **7** · 20.3, 20 5, 20 5, 20 6, 169 0, 169 3, 169.8, 170 5, [b] - The azido group numbering is shown in Fig 1, [c] - These assignments rest on a 2D nmr correlation (HMQC gradient), [d] - These assignments may be reversed, [e] - These assignments follow those determined for compound **3**; [f] - see ref 6.

pair Earlier studies[18] have concluded that the methoxy signal of methyl glucopyranosides is generally deshielded by approximately 0 2 ppm for β anomers as compared to their α counterparts. On this basis, an equatorial orientation was anticipated for the alkoxy groups in **4** and **6** (δ ppm methyl 3 42, **3**, 3 52, **4**, methylene 3 67 and 3 78, **5**, 3 79 and 3 88, **6**) This conclusion was in agreement with nOe difference spectra recorded for **3** and **4** selective irradiation of the methoxy singlets resulted in a 2% enhancement of, respectively, the H-5 (**3**) and H-2 (**4**) signals For the anomer **3**, no enhancement appeared for H-3, probably because of the orientation of the methoxy group towards the endocyclic oxygen atom, as observed for methyl glycosides in solution[19] or in the solid state. However, since compound **3** gave nice crystals, a X-ray structure determination was undertaken in order to unambiguously assign the anomeric configuration of these new compounds

The structure obtained for **3** corroborated the conclusion of the nmr analysis, namely the equatorial orientation of the azido group visible in the PLUTO[20] drawing (Figure 1) It is worth to note that the equatorial azido group is oriented towards the C-2 ring atom whereas the methoxy group is oriented towards the endocyclic oxygen atom Such a conformation differs from those observed in the solid state for two glycopyranosyl azides[21,22] in which the orientation of equatorial azido groups, towards the ring oxygen atom, has been explained by the exo-anomeric effect associated with this group[23] The N–N–N angle (172 5(3)) in **3** is very close from the values found in closely related pyranosyl azides (171 5(6)[21], 172 6(5)[22]) whereas the pyranosyl ring display the usual $^4C_1$-D-chair conformation with each acetyl group in equatorial orientation Positional parameters and their estimated standard deviations, bond distances and bond angles are listed in Tables 3, 4 and 5

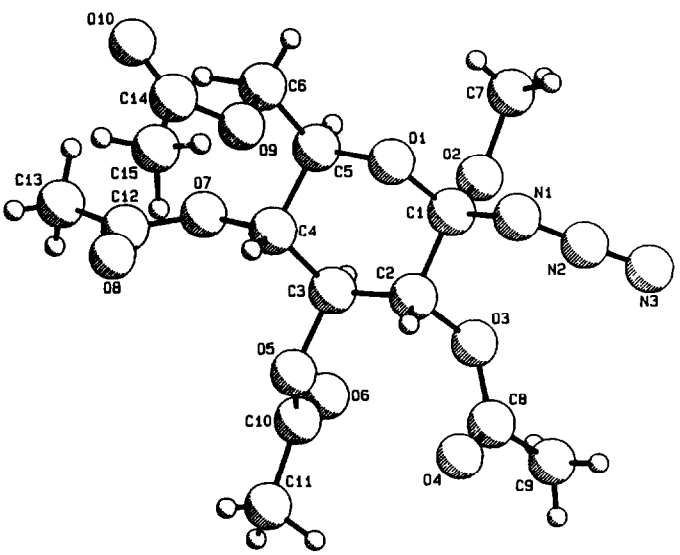


Fig 1. PLUTO drawing of compound **3**

Table 3 Positional parameters and their estimated standard deviations for compound **3**

Atom	x	y	z	B_{eq} (Å^2)
O1	0 0639(1)	0 7652(2)	-0 0202(3)	4 60(5)
O2	0 0898(1)	0 9756(2)	-0 0333(2)	4 59(5)
O3	0 1128(1)	0 9924(2)	0 2542(2)	4 20(4)
O4	0 0888(2)	0 9192(3)	0 4790(3)	7 66(7)
O5	0 2062(1)	0 7913(2)	0 2939(2)	4 26(5)
O6	0 2710(1)	0 9577(3)	0 2824(4)	9 24(8)
O7	0 2339(1)	0 6709(2)	0 0128(3)	4 45(5)
O8	0 2275(1)	0 4822(2)	0 1179(3)	7 45(7)
O9	0 0874(1)	0 5151(2)	-0 0593(3)	6 47(6)
O10	0 1213(2)	0 3639(3)	-0 2034(4)	11 0(1)
N1	-0.0035(1)	0 8964(3)	0 0916(3)	4 95(6)
N2	-0 0181(1)	1 0018(3)	0 1331(4)	5 63(7)
N3	-0 0381(2)	1 0925(3)	0 1724(6)	9 3(1)
C1	0 0656(2)	0 8806(3)	0 0535(3)	3 95(7)
C2	0 1077(2)	0 8699(3)	0 1905(3)	3 69(6)
C3	0 1753(1)	0 8225(3)	0 1556(3)	3 76(6)
C4	0 1700(1)	0 7027(3)	0 0666(4)	3 94(7)
C5	0 1271(2)	0 7232(3)	-0 0677(4)	4 59(7)
C6	0 1163(2)	0 6054(3)	-0 1563(4)	5 72(9)
C7	0 0593(2)	0 9930(4)	-0 1753(4)	7 1(1)
C8	0 1027(2)	1 0047(3)	0 4018(4)	5 00(8)
C9	0 1133(2)	1 1376(4)	0 4463(4)	7 4(1)
C10	0 2518(2)	0 8700(3)	0 3485(4)	5 26(8)
C11	0 2696(2)	0 8354(3)	0 5016(5)	6 28(9)
C12	0 2567(2)	0 5554(3)	0 0443(4)	4 81(8)
C13	0 3213(2)	0 5360(4)	-0 0266(4)	5 92(9)
C14	0 0941(2)	0 3960(4)	-0 0960(5)	6 6(1)
C15	0 0662(2)	0 3140(4)	0 0187(7)	9 0(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = 4/3\ \Sigma_i\Sigma_j\beta_{ij}\ a_i a_j$

Table 4 Bond distances (Å)

O1 — C1	1 409(4)	O7 — C4	1 441(4)	C2 — C3	1 512(4)
O1 — C5	1 439(4)	O7 — C12	1 357(4)	C3 — C4	1 522(4)
O2 — C1	1.380(4)	O8 — C12	1 192(4)	C4 — C5	1 515(5)
O2 —C7	1.440(4)	O9 — C6	1 436(4)	C5 — C6	1 515(5)
O3 — C2	1 441(3)	O9 — C14	1 330(5)	C8 — C9	1 501(5)
O3 — C8	1 355(4)	O10 — C14	1 171(6)	C10 — C11	1.478(6)
O4 — C8	1 188(4)	N1 — N2	1 231(4)	C12 — C13	1 487(5)
O5 — C3	1 441(4)	N1 —C1	1 469(4)	C14 — C15	1 476(7)
O5 — C10	1.354(4)	N2 — N3	1.116(5)		
O6 — C10	1 184(5)	C1 — C2	1 514(4)		

Table 5 Bond angles (°)

C1 — O1 — C5	113 3(2)	N1 — C1 — C2	111 6(3)	O9 — C6 — C5	107 7(3)
C1 — O2 — C7	116.5(3)	O3 — C2 — C1	107 4(2)	O3 — C8 — O4	122.6(3)
C2 — O3 — C8	118 1(2)	O3 — C2 — C3	109 0(2)	O3 — C8 — C9	109 5(3)
C3 — O5 — C10	118 4(2)	C1 — C2 — C3	112 3(2)	O4 — C8 — C9	127 9(3)
C4 — O7— C12	117 5(2)	O5 — C3 — C2	107 6(2)	O5 — C10 — O6	122.9(3)
C6 — O9 — C14	117 1(3)	O5 — C3 —C4	107 0(2)	O5 — C10 —C11	110 8(3)
N2 — N1 — C1	114 4(3)	C2 — C3 — C4	109 3(2)	O6 — C10 — C11	126 2(3)
N1 — N2 — N3	172 5(3)	O7 — C4 — C3	108.3(2)	O7 — C12 — O8	123 2(3)
O1 — C1 — O2	113 1(2)	O7 — C4 — C5	107.1(3)	O7 — C12 — C13	110 2(3)
O1 — C1 — N1	100 9(2)	C3 — C4 — C5	110 0(3)	O8 — C12 — C13	126 6(3)
O1 — C1 — C2	109 5(2)	O1 — C5 — C4	109 3(3)	O9 — C14 — O10	122 6(4)
O2 — C1 — N1	113 3(2)	O1 — C5 — C6	106 7(3)	O9 — C14 — C15	111 1(4)
O2 — C1 — C2	108 4(2)	C4 — C5 — C6	112 8(3)	O10 — C14 — C15	126 2(4)

Including the known peracetylated β and α-D-glucopyranosyl azides **8**[23] and **9**[24], the series **3-9** comprises three anomeric pairs of monoazido derivatives and one *gem* diazide Such compounds appeared suitable models for a comparative ^{15}N nmr study In effect, deshieldings have been observed for equatorial nuclei attached at C-1, such as ^{1}H [25], ^{19}F [26,27], ^{13}C [28] in pyranose derivatives displaying a $^{4}C_1$-D chair conformation It was anticipated that the nitrogen nuclei of the azido group might behave similarly To this end, the ^{15}N nmr spectra[29] of compounds **3**, **4**, **7**, **8** and **9** in normal chloroform solutions were recorded As seen in Table 2, each nitrogen nucleus in the azido group give well resolved signals over a range of about 160 ppm While the chemical shifts of the central nitrogen nuclei are practically unaffected by the anomeric configuration, as seen for the β and α-D-glucopyranosyl azides **8** and **9**, both lateral nitrogen atoms experience a deshielding effect when the azido group has an equatorial orientation This effect is larger (4 5 to 6 4 ppm) for the simple glucopyranosyl azide **8**, as compared to C-1 disubstituted derivatives (2 0 to 3 6 ppm) The nitrogen resonances observed for **7** have been tentatively assigned following the preceeding observations

In conclusion, the synthesis of epimeric peracetylated methyl or ethyl D-glucopyranosides substituted at C-1 by an azido group can be readily carried out from the corresponding anomeric orthoesters on treatment with trimethylsilyl azide and boron trifluoride etherate In both cases, the compound with a 1(*R*) anomeric configuration (β-N_3, α-alkoxy) was isolated in higher amount (~60 % yield) as result of the *in situ* anomerization of the 1(*S*) kinetic product (20-25% yield) In the solid state, the axial methoxy group and the equatorial azido group in **3** are oriented, respectively, towards the ring oxygen and the C-2 carbon atoms A comparative ^{15}N nmr study showed that both lateral nitrogen nuclei in equatorial azido groups are deshielded as compared to axial ones The photolysis of these new highly functionalised sugar derivatives will be reported in due course

Acknowledgement The authors are thankful to Dr B L Zhang (University of Nantes) for his help in the ^{15}N nmr study

EXPERIMENTAL

General methods Melting points, measured with a Buchi-Tottoli apparatus are not corrected. Optical rotations were determined with a PERKIN ELMER 241 polarimeter IR spectra were recorded with a PERKIN ELMER spectrophotometer Thin-layer chromatography and column chromatography were performed with silica gel (Kieselgel 60F $_{254}$ and Kieselgel 60 Merck) Dichloromethane and acetonitrile used for synthetic runs were distilled over CaH_2. ^1H and ^{13}C nmr spectra were recorded with a BRUKER AM 300 spectrometer for deuteriochloroform solutions containing tetramethylsilane as the internal reference A BRUKER AM 400 spectrometer was used for measuring the ^{15}N nmr spectra (approximately 1 g of sugar azide in 5 mL of chloroform containing ~50 mg of chromium (II) acetylacetonate as relaxation agent) using nitromethane as the external reference (15 mm tubes) Compounds **1** and **2** have been prepared by known procedures[7]

Methyl 1-azido-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside 3 and methyl 1-azido-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside 4 A mixture of orthoester **1** (2 72g, 6 9 mmol) in dichloromethane (35 mL) was stirred, at room temperature for 24h, under a nitrogen atmosphere, in the presence of trimethylsilyl azide (4 6 mL, 34 6 mmol) and boron trifluoride etherate (0 87 mL, 6 9 mmol) Tlc monitoring (n-hexane-ethyl acetate 6 4 v/v) showed two new, slightly less polar spots corresponding to only two products as indicated by ^1H nmr analysis of the crude reaction mixture After washing the organic phase with a saturated $NaHCO_3$ solution (3*30 mL) then water (3*30mL) and drying over Na_2SO_4, the organic phase was concentrated under reduced pressure The residue (2 8g) was resolved by column chromatography (n-hexane-ethyl acetate 2 1 v/v) to yield pure **4** (0 55 g, 20 % yield) and **3** (1 76 g, 63 % yield) as crystalline solids Synthetic runs using acetonitrile as the solvent were conducted similarly, but in the presence of variable amounts of boron trifluoride etherate (see Table 1)

3 mp 86-88°C (diethyl ether-petroleum ether), $[\alpha]_D$ + 15° c, 0 4 chloroform, ν N_3 2130 cm^{-1},

Anal Calc for $C_{15}H_{21}N_3O_{10}$ C, 44 67, H, 5 25, N, 10 42, O, 39 67 Found C, 44 86, H, 5 33, N, 10 42, O, 39 59

4 mp 77-78°C (diethyl ether-petroleum ether), $[\alpha]_D$ + 99° c, 0 8 chloroform, ν N_3 2130 cm^{-1},

Anal Calc for $C_{15}H_{21}N_3O_{10}$ C, 44 67, H, 5 25, N, 10 42, O, 39 67 Found C, 44 53, H, 5 23, N, 10 64, O, 39 76

Anomerization of 4 A sample of pure **4** (10 6 mg) was stirred at room temperature in dry dichloromethane (1mL) in the presence of trimethylsilyl azide (17 3μL) and boron trifluoride etherate (3 3μL) for 70 mn Tlc examination suggested that a mixture of predominantly **3** and **4** was obtained After aqueous workup, the residue (9 5mg) was shown by ^1H nmr to contain only **3** and **4** (71/29)

Ethyl 1-azido-2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside 5 and ethyl 1-azido-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside 6 The procedure used for the preparation of **3** and **4** in dichloromethane allowed the synthesis of azido ethyl glucosides **5** and **6** in comparable yields Compound **6** was eluted before **5**, in particular when using a mixture of n-hexane-ethyl acetate 8 2 v/v for column chromatography

5 mp 65-66 °C (diethyl ether-petroleum ether), $[\alpha]_D$ + 22° c, 0 8 chloroform, ν N_3 2130 cm^{-1}

Anal Calc for $C_{16}H_{23}N_3O_{10}$ C, 46 04, H, 5 55, N, 10 07, O, 38.33 Found· C, 46 19, H, 5 60, N, 9 77, O, 37 95

6 $[\alpha]_D$ + 90° c, 1 1 chloroform, ν N_3 2130 cm^{-1}

Anal Calc for $C_{16}H_{23}N_3O_{10}$ C, 46 04, H, 5 55, N, 10 07, O, 38 33 Found C, 45 41, H, 5 60, N, 9 58, O, 37 61

X-ray crystal structure determination of 3 Colourless crystals were obtained from diethyl ether-petroleum ether A crystal of 0 4*0 4*0 1 mm was mounted on a Nonius CAD-4 diffractometer at 20°C, using CuKα radiation (graphite monochromator) Unit cell parameters were refined from setting angles of 25 selected reflections (18 2 < 2θ < 48 0°) The crystals are orthorhombic, space group $P2_12_12_1$ with a = 9 033(1), b = 10.755(1), c = 20 527(2)Å, V = 1994 3(6)Å^3, M_r = 403 3 for $C_{15}H_{21}N_3O_{10}$, D_x = 1 344 g cm^{-3}, Z = 4, μ(λCuKα) = 10 cm^{-1} Intensity data were collected using ω-4/3 θ scan A total of 2008 independent reflexions were measured and only 1711 were considered as observed (I > 3σ(I)) The structure was solved using MULTAN and refined by full-matrix least squares based on F All the hydrogen atoms were located from Δf syntheses and assigned with an isotropic thermal parameter equal to 4.0. The final agreement indice was R = 0 035 All the calculations were carried out on a Microvax II computer using the Enraf Nonius SDP[30] system. Atomic coordinates and equivalent isotropic thermal parameters are in Table 3 and main bond lenghts and angles in Tables 4 and 5 Lists of structure factors, anisotropic thermal parameters, H-atom coordinates have been deposited at the Cambridge Crystallographic Data Centre

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